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Frederick Noel Ashcroft.

By W. CAMPBELL SMITH.

FREDERICK NOEL ASHCROFT was Treasurer of the Society from 1924 to 1942, President 1942-45, Foreign Secretary from 1947, and one of the Society's two Trustees from 1911 until his death. This occurred quite suddenly at his home in London on 4 April 1949. He would have been 71 on the 28th of August of that year. Most of the details of his life and work are recorded in an obituary notice in the 'Quarterly Journal of the Geological Society' (1950, vol. 105, pp. lxix-lxxii), but it seems fitting that his work should receive some special mention in the pages of our own Journal, for in his long service he did much for the Society by his careful management of its affairs, and by his mineral collecting and his generous gifts to the British Museum he made a substantial contribution to our Science.

The membership when Ashcroft became Treasurer was only 180 and it had increased only by 87 at the beginning of the war in 1939. The annual income at that time was no more than £750, so the keeping of the accounts was a small matter to one of Ashcroft's calibre. However, he took his duties very seriously and any member who had not signed a banker's order or become a Life Member was certain to receive a reminder that his subscription was due, addressed in Ashcroft's own hand and posted on New Year's Eve! The bills for printing the Magazine and the statements of sales were always scrutinized with the greatest care, and he kept a close check on the stock of back numbers. In this connexion he made quite a hobby of buying up runs of the Magazine whenever he could, and he used these to make up sets to meet the needs of mineralogists and libraries at home and abroad. In many unobtrusive ways he helped the Society financially, and much of the expense he incurred in the office work on the Society's accounts he bore himself without ever letting the extent

of his expenditure be known. In its Honorary Treasurer as well as in its Honorary Editor the Society was undoubtedly remarkably well served.

As a mineralogist Ashcroft did little detailed research and published little, but he was a very keen collector and indefatigable in his labelling and cataloguing, and he has left in the Department of Mineralogy of the British Museum (Natural History) three collections each of which in its own field is unrivalled for fine quality of specimens and for wealth of detail as to locality and mineral associations.

Ashcroft's mineral collecting began while he was at Oxford where he had entered Magdalen College from Rugby in 1897. He accompanied [Sir Henry] Miers, then Professor of Mineralogy at Oxford, on excursions with his students to British mineral localities, and in 1901 he joined [Sir] Harold Hartley on a mineral-collecting visit to the Seiser Alpe in the Tyrol.

At first Ashcroft specialized on zeolites and between 1901 and the outbreak of the First World War he had assembled a collection of some 2000 specimens from about 80 localities, chiefly in Europe and America. This collection he presented to the British Museum in 1914, intending to concentrate his own attention on the zeolites of the Tertiary basalts of Northern Ireland of which he had already made a considerable collection. In this work he had already enlisted the interest of two well-known Belfast naturalists, Robert Bell, a geologist and mineralogist, and R. J. Welch, well known at that time for his geological, botanical, and zoological photographs. When Ashcroft's own visits to Ireland became impracticable owing to the outbreak of war Bell continued to visit the working quarries and to collect the zeolites, dispatching specimens from time to time to Ashcroft in London. As a result Ashcroft acquired a remarkably fine collection of specimens from about 90 localities, chiefly in County Antrim. Every available detail was recorded in manuscript catalogues, and photographs by R. J. Welch of the quarries and cliff sections are filed in loose-leaf books.

Ashcroft intended working up the material in this collection himself but this he never had time to do, and under the terms of his will it passed to the British Museum (Natural History) at his death. His only published works on the zeolites were two papers by himself and topographical notes contributed to a paper by G. F. Herbert Smith on chabazite and associated minerals from County Antrim in the 'Mineralogical Magazine' for 1916.

The largest and best known of Ashcroft's three collections is his collection of Swiss minerals. This he commenced soon after the First World

War. During yearly visits to Switzerland he came to know all the leading mineralogists and the local mineral collectors. From the collectors, many of them expert Alpine guides, he purchased great numbers of fine specimens, but it was a condition he made that for every specimen he must be able to ascertain the exact locality and if possible to see and examine each locality himself. He insisted that if the paragenesis of the minerals was to be thoroughly studied, it was essential that specimens from neighbouring fissures, even if situated only a few feet apart, must be kept separate.

His principal collecting areas centred about Disentis and Sedrun in the Vorder Rhein Valley and about Andermatt and Amsteg. From the last two places he could reach not only the mineral localities accessible from the Reuss Valley but also those in the St. Gotthard district, in Urseren Thal, Göschenen Thal, and in Maderaner Thal. He was in frequent correspondence with Franz Indergand of Ried by Amsteg and others of the Indergand family in that district and in Göschenen. His most constant correspondents, and the two who seem to have been the most helpful of the local collectors in and around Tavetsch Thal, were Adolf Caveng, the postmaster at Sedrun, and his son Ambrosi. Ashcroft's practice was to send maps to the Indergands and to the Cavengs on which the sites of any finds they made could be marked. In the following summer he would visit the localities himself accompanied by the collectors and would photograph the sites. Prints of these photographs were then used to pin-point the finds more precisely and to record any further finds there might be. For this work he used a half-plate stand camera with a heavy tripod stand. He considered smaller negatives did not give him suitable reproductions for his purpose and the stand needed to be suitable for use on steep, rough ground. With this heavy equipment he travelled considerable distances in the mountains and he went to great trouble to get to positions from which to photograph every accessible site.

Much of the accurate information he obtained about the Swiss minerals and their paragenesis he contributed to 'Die Mineralien der Schweizeralpen' by Niggli, Koenigsberger, and Parker (1940), and 16 plates in that work are reproductions of Ashcroft's photographs. Some others of his photographs appear as plates in Holmes's 'Principles of Physical Geology' (1944).

The whole of the Swiss collection of over 6000 specimens was presented to the British Museum between 1921 and 1938 and the catalogues and the negatives and prints of all his photographs connected with the

collections have now also passed to the Museum under the terms of his will. He also left in trust a sum of £100 for the purpose of completing the catalogues of his mineral collections.

Besides these collections Ashcroft presented many other specimens to the British Museum: specimens from the Tyrol in 1903; a fine selection purchased from the Walker Collection in 1912; minerals from Wales, Derbyshire, the Lake District, and Cumberland collected on short holidays with his family during the First World War; and a fine series of specimens of minerals from Broken Hill, Rhodesia, partly collected by himself on a visit to the mine during an excursion of the International Geological Congress in 1929 and added to on a separate visit by Mr. D. W. Bishopp, then curator of the Rhodesia Museum.

The value of his contributions to our national collection of minerals is not to be measured by numbers of specimens, but the total is close on ten thousand. Ashcroft's gifts to the Museum far exceed those of any other single benefactor of the Department of Mineralogy up to the present time.

Under his will he left his complete sets of the 'Mineralogical Magazine,' the 'American Mineralogist,' and the 'Schweizerische Mineralogische und Petrographische Mitteilungen' to the Society together with the sum of £150 with the sole proviso that it be not 'used for the purpose of providing any prize or medal or a reward of any sort to individual persons'. Selections of his other mineralogical books were left to the Department of Mineralogy of the British Museum and the Geological Society of London, and others were given to the Department of Geology and Mineralogy at Oxford and to University College, London.

Ashcroft had travelled extensively in France, Germany, Austria, Italy, and Sicily, as well as to South Africa and Rhodesia on the Geological Congress of 1929 and on two holidays with his family to Nova Scotia where the famous zeolites had always an attraction. He had made many friends in many lands among mineralogists and geologists. With the mineral collectors and guides in Switzerland he was on the happiest terms, and a warm welcome awaited him and any members of his family on his arrival in their districts for his annual visit. Robert Bell of Belfast he held in special regard and he kept up a correspondence with him long after they had ceased to collect the Irish zeolites. Letters to Ashcroft from Robert Bell and from the Cavengs are full of references to generous and kindly acts such as Ashcroft never spoke of but was always doing for his friends.

He married in 1904 Constance Muriel, daughter of J. C. im Thurn, and

their family life was a very happy one. Ashcroft was justly proud of his sons and daughters and devoted to them, and in later years to his grandchildren. Our portrait (plate VII) shows him with two of his grandsons in the garden of a house in Oxford he occupied during some of the years of the last war.

It is six years now since his passing but his memory is fresh among us. He will not soon be forgotten and his mineral collections will remain always as his memorial.

*Determination of the composition of kalsilites by
an X-ray method.*

By TH. G. SAHAMA,

Professor of Geochemistry, Institute of Geology, Helsinki, Finland,

K. J. NEUVONEN, Ph.D.,

Geological Survey, Helsinki, Finland,

and KAI HYTÖNEN, M.A.,

Institute of Geology, Helsinki, Finland.

[Read 26 January 1956.]

Summary.—Three new analyses of kalsilite are given, with optical and X-ray data; two ($K/(K+Na) = 0.95, 0.98$) are from rocks where it is closely associated with nepheline. An analysis of one of the nephelines is also given ($K/(K+Na) = 0.31$). The cell dimensions vary appreciably with sodium content, and the composition of kalsilite may be determined from the equation:

$$100 K/(K+Na) = 100 - 227.27(\Delta - 6.264),$$

where Δ is the difference, in degrees, between the diffraction angles 2θ for $10\bar{1}2$ and $10\bar{1}1$, using Cu- $K\alpha$ radiation.

THE variation of optical properties with chemical composition in the nepheline and kalsilite series is very slight. Accordingly, for determining the nepheline composition in petrographic rock description, optical methods will fail. On the other hand, a change in the ratio of potassium to sodium in nepheline is accompanied by a considerable change in the unit-cell dimensions. This fact offers a possibility for rapid determination of the nepheline composition by measuring the spacings of suitable powder diffraction lines. Such an X-ray method was successfully developed by Smith (1956) for synthetic materials and was later applied by Smith and Sahama (1954) to natural nephelines. This method allows a fairly accurate determination of the potassium content, expressed in atomic per cent, $100 K/(K+Na+Ca)$.

As in nepheline, powder diffraction data may be used for determining the ratio of potassium to sodium in kalsilite. In his paper mentioned above, Smith (loc. cit.) gives the difference in 2θ angle between the kalsilite lines $10\bar{1}2$ and $10\bar{1}1$. The measurements were made using copper radiation. No internal standard is needed. The difference, Δ , is

thus defined as follows: $\Delta = 2\theta_{(10\bar{1}2)} - 2\theta_{(10\bar{1}1)}$. The Δ -values were given by Smith for two synthetic kalsilite preparations that contained 90 and 100 % by weight KAlSiO_4 , respectively. Assuming that the Δ -value varies linearly with the composition, these data may be used for determining the composition of kalsilite.

For natural kalsilite, the rarity of the mineral has, so far, made systematic measurements of Δ -values impossible. In literature, only three localities are known from which kalsilite has been studied physically and chemically: San Venanzo in Italy (Bannister, Sahama, and Wiik, 1953), Mafuru-Kyambogo crater in Uganda (Bannister and Hey, 1942; Sahama, 1954), and Nyiragongo area in the Belgian Congo (Sahama, 1953).

The last-mentioned area was visited by the authors in 1952. Kalsilite was found in one single flow that was later called the Kabfumu lava. In 1954 two of the authors (Th. G. S. and K. H.) paid a new visit to the Nyiragongo area and found several new localities with lavas containing kalsilite. Especially important in this connexion are the lavas of the extinct crater of Baruta, the great northern tributary of the active main crater of Mt. Nyiragongo. In Baruta several kalsilite-bearing rocks were found. Among the lavas collected, two specimens were selected from which kalsilite could be separated with heavy liquids, &c.

The availability of these two new kalsilite specimens made it possible to test the applicability of Smith's data for synthetic materials to natural kalsilite. For the petrology of the rare kalsilite-bearing lavas, like those of the Nyiragongo area, such a test is of a certain importance. The mode of occurrence of kalsilite in the Nyiragongo area will be described later by one of the authors (Th. G. S.) in the papers published by the Institut des Parcs Nationaux du Congo Belge in Brussels. In this paper only some physical and chemical data for kalsilite will be given.

The specimens.

The following specimens were available for the present study:

1. Synthetic kalsilite from blast-furnace lining. Original specimen investigated by Rigby and Richardson (1947) and Jay and Andrews (1947). The specimen, placed at the authors' disposal by Dr. G. R. Rigby, of the British Refractories Research Association, Stoke-on-Trent, was subjected to a heavy liquid separation with Clerici's solution and centrifuge. Of the purified material, virtually free of any contamination, a new chemical analysis was made by Dr. H. B. Wiik, of the Geological Survey of Finland, Helsinki. The result of the analysis (table

I) shows the material to be a pure kalsilite without any sodium component. The powder pattern¹ shows no foreign lines.

2. Specimen numbered S. 88. South-eastern part of the outer rim of Baruta crater, Nyiragongo area, Belgian Congo. The rock contains complex phenocrysts with kalsilite kernel and nepheline margin (fig. 1,

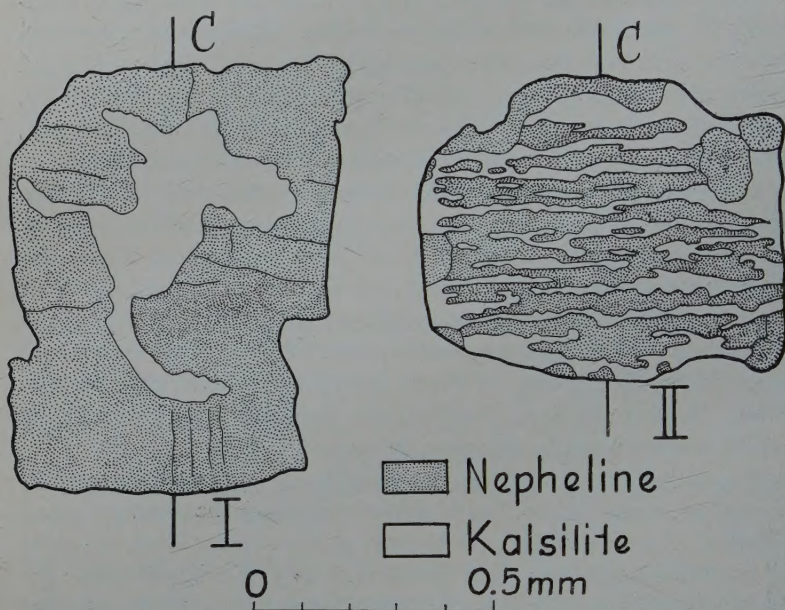


FIG. 1. Complex phenocrysts of nepheline and kalsilite in the lavas of Baruta crater, Nyiragongo area, Belgian Congo. I. Specimen S. 88. Kalsilite kernel surrounded by a nepheline margin. No sign of perthitic exsolution. II. Specimen S. 96 = M. 25. Perthitic exsolution of nepheline in kalsilite.

I). No sign of perthitic exsolution is visible. By a heavy liquid (Clerici's solution and centrifuge) and magnetic (Frantz-type isodynamic separator) separation, the complex phenocrysts were isolated from the rock, ground down to a grain size of *c.* 0.01 mm., and subjected to a final heavy liquid separation.

In the powder pattern of the best nepheline fraction the very sensitive kalsilite line $10\bar{1}2$ could not be traced. Accordingly, the kalsilite content of the material must be less than *c.* 1 % by weight. This nepheline material was analysed by Mr. Pentti Ojanperä of the Geological Survey

¹ The powder patterns used in this work were recorded with a Philips X-ray diffractometer ('Norelco') and copper radiation.

of Finland, Helsinki, with the following result: SiO_2 41.08, TiO_2 0.07, Al_2O_3 33.41, Fe_2O_3 0.96, FeO 0.18, MnO 0.01, MgO 0.13, CaO 0.18, Na_2O 14.02, K_2O 9.70, CO_2 0.00, $\text{H}_2\text{O} +$ 0.26, $\text{H}_2\text{O} -$ 0.02, total 100.02. The analysis gives a composition of 31.1 atomic % $\text{K}/(\text{K} + \text{Na} + \text{Ca})$. Of the powder pattern, the lines $20\bar{2}2$ and $21\bar{3}0$ were measured. The results, $2\theta_{(20\bar{2}2)} = 29.550^\circ$ and $2\theta_{(21\bar{3}0)} = 27.130^\circ$, indicate a composition of 31.5 and 30.7 atomic % $\text{K}/(\text{K} + \text{Na} + \text{Ca})$, respectively. The composition deduced from the X-ray measurements is virtually identical with that calculated from the analysis. This fact represents a further proof of the purity of the nepheline analysed.

The powder pattern of the kalsilite fraction obtained in the separation showed the presence of the strongest nepheline lines. According to preliminary tests, 4 % by weight of nepheline in kalsilite could still be qualitatively detected with the apparatus used. The absence of all the nepheline lines from a powder pattern of kalsilite would, therefore, only indicate the nepheline contamination to be less than that amount. The amount of contamination in the low nepheline contents could, accordingly, not be accurately determined. For this reason, no attempt was made to remove nepheline from the kalsilite fraction completely. In the kalsilite material, intended for chemical analysis, enough nepheline was left behind to ensure accurate determination of its amount. It was found that, if more than 7 % nepheline is present in kalsilite, the intensities of the strongest nepheline lines are sufficient for a quantitative determination of the amount of nepheline contamination.

For quantitative determination of the amount of nepheline contamination in kalsilite, a series of standard mixtures was prepared of pure nepheline and pure kalsilite. The mixtures contained 7.0, 11.1, 15.0, 20.0, and 30.3 % by weight nepheline in kalsilite, respectively. All mixtures were thoroughly homogenized. Of each mixture, powder patterns were recorded six times. Between two runs the slide was slightly shifted so that a new spot came into the reflecting position. The intensities of nepheline $20\bar{2}2$ and of kalsilite $10\bar{1}3$ and $11\bar{2}1$ were measured in the chart. The intensities of all these lines were found to fall within the linear range of the recorder. The following intensity ratios were calculated and plotted against weight % nepheline in kalsilite: $I_{\text{Ne}(20\bar{2}2)} / (I_{\text{Ks}(10\bar{1}3)} + I_{\text{Ne}(20\bar{2}2)})$ and $I_{\text{Ne}(20\bar{2}2)} / (I_{\text{Ks}(11\bar{2}1)} + I_{\text{Ne}(20\bar{2}2)})$. Six runs were made of the kalsilite material from specimen S. 88 as prepared for analysis; the averages of the above intensity ratios were calculated and the corresponding nepheline content read from the standard diagram. The results indicated a nepheline content of 9.2 and 10.8 % by weight,

respectively. The average, 10.0 % by weight, is believed to be correct within ± 1 %. Chemical analysis of the fraction made by Mr. Ojanperä gave the following results: SiO_2 38.68, TiO_2 0.06, Al_2O_3 31.20, Fe_2O_3 (total iron) 1.13, MnO 0.01, MgO 0.00, CaO 0.05, Na_2O 1.67, K_2O 26.42, CO_2 0.00, $\text{H}_2\text{O}+$ 0.63, $\text{H}_2\text{O}-$ 0.07, total 99.92.

Now, knowing the composition and amount of nepheline in the kalsilite fraction of specimen S. 88 as well as the total composition of this fraction, the composition of the pure kalsilite phase may be calculated. The result is given in table I and is believed to be of an accuracy not far behind a direct chemical analysis.

3. Specimen numbered S. 96 = M. 25. Fallen block on the bottom of the Baruta crater, Nyiragongo area, Belgian Congo. The rock contains phenocrysts of kalsilite perthite (fig. 1, II) in which the perthitic structure is unusually coarse thus making a heavy liquid separation possible. As in the case of the previous specimen (S. 88), kalsilite could not be obtained in a pure fraction from specimen S. 96. Therefore, the amount and composition of the nepheline contamination was determined in the final material that had been accepted for chemical analysis and the result of the analysis was corrected for this nepheline contamination. The result of the chemical analysis made by Mr. Ojanperä is as follows: SiO_2 38.70, TiO_2 0.06, Al_2O_3 32.12, Fe_2O_3 (total iron) 0.98, MnO 0.01, MgO 0.00, CaO 0.03, Na_2O 3.85, K_2O 23.85, CO_2 0.00, $\text{H}_2\text{O}+$ 0.37, $\text{H}_2\text{O}-$ 0.03, total 100.00. The intensity ratios of the powder lines of nepheline and kalsilite mentioned above in connexion with the previous specimen were calculated. The results indicate a nepheline content of 22.2 and 23.2 % by weight, respectively. The average, 22.7 % by weight, is again believed to be correct within ± 1 %. The 2θ angles of the nepheline lines $20\bar{2}2$ and $21\bar{3}0$ are: $2\theta_{(20\bar{2}2)} = 29.560^\circ$ and $2\theta_{(21\bar{3}0)} = 27.145^\circ$. These values correspond to 30.7 and 29.6 atomic % $\text{K}/(\text{K} + \text{Na} + \text{Ca})$ in nepheline. The average, 30.2 atomic % $\text{K}/(\text{K} + \text{Na} + \text{Ca})$, was adopted. According to these X-ray data, the composition of the nepheline contamination in the analysed kalsilite material of specimen S. 96 is very close to the composition of nepheline of specimen S. 88. Therefore, in correcting the analysis of the kalsilite material given above for the nepheline contamination, the nepheline phase was assumed to have a composition that is shown by the nepheline analysis of specimen S. 88. The composition of the kalsilite phase of specimen S. 96, corrected for nepheline contamination, is given in table I.

4. San Venanzo, Italy. Original specimen investigated by Bannister, Sahama, and Wiik (1953). Analysis reproduced in table I.

5. Kyambogo crater, Bunyaruguru field, Uganda. Original specimen investigated by Sahama (1954). Analysis reproduced in table I.

TABLE I. Chemical analyses of kalsilite.

	1.	2.	3.	4.	5.
	Synthetic.	Baruta S. 88.	Baruta S. 96.	San Venanzo.	Kyambogo FEAE 41.
SiO ₂	37.89	38.48	37.98	38.47	38.50
TiO ₂	0.19	0.05	0.05	0.00	0.09
Al ₂ O ₃	32.60	31.01	31.73	30.81	26.27
Fe ₂ O ₃	1.26	1.12*	0.98*	1.63	5.07
FeO	0.00	n.d.	n.d.	0.26	0.53
MnO	0.01	0.01	0.01	0.00	0.02
MgO	0.29	0.00	0.00	0.63	0.87
CaO	0.21	0.03	0.00	0.20	0.44
Na ₂ O	0.00	0.30	0.87	2.09	2.07
K ₂ O	27.88	28.33	27.99	25.65	24.85
H ₂ O+	0.00	0.67	0.40	0.20	1.04
H ₂ O-	0.00	—	—	0.00	0.05
Total	100.33	100.00	100.01	99.94	99.80

* Total iron as Fe₂O₃.

Physical properties.

The physical properties of the kalsilite specimens have been collected in table II. The unit-cell dimensions have all been converted from kX to Å. For the values of *a* and *c* not previously published, the uncertainties are given as estimated. The Δ -values are expressed in degrees. Each

TABLE II. Physical properties of kalsilite.

$\Delta = 2\theta_{(10\text{I}2)} - 2\theta_{(10\text{I}1)}$, using Cu-K α radiation.

	1.	2.	3.	4.	5.
	Synthetic.	Baruta S. 88.	Baruta S. 96.	San Venanzo.	Kyambogo FEAE 41.
Sp. gr.	n.d.	n.d.	n.d.	2.625	2.663
ϵ	1.532	1.533	1.534	1.537	1.550
ω	1.538	1.539	1.539	1.543	1.554
<i>a</i>	5.161*	5.161 $\pm$ 0.004	5.160 $\pm$ 0.002	5.151	5.165 $\pm$ 0.003
<i>c</i>	8.702*	8.693 $\pm$ 0.005	8.689 $\pm$ 0.002	8.673	8.668 $\pm$ 0.004
Δ	6.264°	6.274°	6.284°	6.317°	6.313°
100 K					
K+Na+Ca	100.0	98.3	95.0	88.5	87.6

* Determined by Jay and Andrews (1947).

Δ -value represents an average of six runs. With the same apparatus and following exactly the same procedure, the accuracy of the Δ -values is believed to be better than $\pm 0.01^\circ$, probably of the order of $\pm 0.005^\circ$.

This would correspond to an accuracy of 1 atomic % $K/(K+Na+Ca)$.

The unit-cell dimensions and the Δ -values of table II have been plotted against the composition in fig. 2. This figure includes also the following data for synthetic kalsilite given by Smith (1955): Ks_{100} , a 5.160 ± 0.002 ,

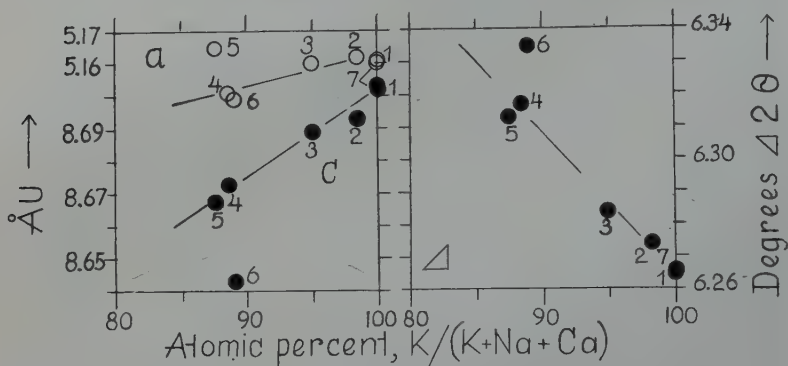


FIG. 2. Unit-cell dimensions and Δ -values for kalsilite plotted against composition. The numbers correspond to the specimens in table I. No. 6 denotes the synthetic kalsilite $Ks_{89.0}$ and no. 7 the pure kalsilite Ks_{100} investigated by Smith.

c 8.703 ± 0.002 Å., Δ 6.265° ; $Ks_{89.0}$,¹ a 5.149 ± 0.002 , c 8.643 ± 0.002 Å., Δ 6.335° .

With a reasonable accuracy, the unit-cell dimensions vary linearly with the composition. There are, however, two exceptions. First, the a for the Kyambogo kalsilite is larger than presupposed by the linear relationship between a and composition. This deviation might be explained by the fact that the Kyambogo kalsilite has about 5 % Fe_2O_3 replacing Al_2O_3 . Second, the value for c of the synthetic kalsilite $Ks_{89.0}$ is low.

Dr. J. V. Smith informs us that there is some doubt about the purity of the two synthetic kalsilites. They were prepared from charges that had been originally crystallized at a high temperature. Recrystallization under hydrothermal conditions by Professor O. F. Tuttle gave a mixture of kalsilite and subordinate leucite. The presence of leucite shows that there has been loss of potassium in the charge. Loss of potassium would not change the K_2O/Na_2O ratio of the kalsilite prepared from a charge of original composition $Ks_{100}Ne_0$. Differential loss of potassium with respect to sodium could decrease the K_2O/Na_2O ratio of the kalsilite prepared from the charge of original composition $Ks_{90}Ne_{10}$. In accordance with this, the values of a and c obtained by Smith for the

¹ Corresponding to 90 % Ks (= $KAlSiO_4$) by weight.

soda-free kalsilite agree very closely with the other values obtained in this work whereas the value for the soda-containing synthetic kalsilite deviates in the direction of higher soda-content. There is no need to suppose that this deviation is a result of a difference in structure between natural and synthetic kalsilites, though this is a theoretical possibility, especially as there may be an order-disorder effect between the Si and Al atoms similar to that found in feldspars.

Being the difference in reflection angles of the lines $10\bar{1}2$ and $10\bar{1}1$ for Cu- $K\alpha$ radiation, the Δ -value depends only on c . Accordingly, the Δ -value for synthetic kalsilite of composition $Ks_{89.0}$ is off the straight line indicated in fig. 2. This straight line satisfies the equation $Ks = 100 - 227.27 (\Delta - 6.264)$. In this equation, Ks denotes the atomic % K/(K + Na + Ca) and Δ denotes the Δ -value measured for the kalsilite the composition of which is to be determined. This equation is recommended for determining the composition of kalsilite by X-rays. The scarcity of the data for natural kalsilite does not allow a statistical estimation of the accuracy of the method.

ADDENDUM.

Since this paper was written, Dr. J. V. Smith has very kindly tested the two soda-rich kalsilites, no. 4 (San Venanzo) and no. 5 (Kyambogo), for a possible nepheline contamination. The tests were made by step-counting on a diffractometer, counting for 5 minutes at angular spacings of 0.025° in 2θ across the position of the strong nepheline peaks. To reduce the background scatter, a rotating specimen holder was used. Kalsilite no. 4 showed small peaks at 29.5 , 27.0 , and 22.9° which indicated the presence of small amounts of nepheline. On the other hand, kalsilite no. 5 was found to be free of nepheline. Dr. Smith also calculated the possible effect of iron on the lattice parameters. Taking the distances Si-O = $1.60 \text{ \AA}$, Al-O = $1.78 \text{ \AA}$, and Fe-O = $1.90 \text{ \AA}$, and assuming that all tetrahedral sites are filled and that the variation of the lattice parameters a and c is proportional to the size of the tetrahedra, he transformed our observed lattice parameters to calculated values for compositions with Si/Al = 1 and Fe = 0. He found the following calculated values:

Kalsilite no. 1.	a 5.158	c 8.697	a^2c 231.39
2.	5.161	8.693	231.54
3.	5.157	8.684	230.95
4.	5.145	8.663	229.32
5.	5.153	8.648	229.63
Ks synthetic 100 %	5.160	8.703	231.72
Ks synthetic 89 %	5.149	8.643	229.15

The most accurate comparison should be with the values of a^2c . If these are plotted against atomic % $K/(K+Na+Ca)$, quite a good straight line may be drawn through the points; kalsilite no. 5 is a little high and Ks synthetic 89 % is a little low. It seems that the discrepancy between some of the data for kalsilites nos. 4 and 5 and, on the other hand, Ks synthetic 89 % may be resolved by invoking the operation of the three factors: change of composition of the synthetic preparation, iron content, or presence of nepheline. Accordingly, the equation for calculating the kalsilite composition given above might yield slightly too low values for the atomic % $K/(K+Na+Ca)$ in the range around 90 %. The authors are very grateful to Dr. Smith for this additional information.

Acknowledgements.—The authors are indebted to Dr. G. R. Rigby for the specimen of synthetic kalsilite, to Dr. H. B. Wiik and to Mr. Pentti Ojanperä for the chemical analyses, and to Dr. J. V. Smith for placing a copy of the manuscript for his forthcoming paper at the authors' disposal.

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Experimental and theoretical studies of the mica polymorphs.

(With Plates VIII and IX.)

By J. V. SMITH, M.A., Ph.D., and H. S. YODER, Jr., S.B., Ph.D.

Geophysical Laboratory, Carnegie Institution of Washington,
Washington, D.C., U.S.A.

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Summary.—An experimental and theoretical study has been made in order to determine the number and the structure of the possible polymorphs and to determine the structural relations between them. The simplest structures are 1M, 2M₁, 2M₂, 3T, 2O, and 6H polymorphs, and more complicated types can be developed. Some of the previously described polymorphs were not contained in the theoretical list and were re-examined. The 6M structure was found to be a 2M₂ polymorph, the 6-layer triclinic type was found to be a 2M₁ polymorph, and the 3M structure was shown to be a 3T type. The 24-layer triclinic structure could be described on a simpler 8-layer cell. This type together with a new 12-layer monoclinic structure, as well as other structures of higher periodicity, presumably consists of complex stacking and results from spiral-growth mechanism. Two extreme types of layer-disordered crystals may be built and a disorder of individual ions may also occur. Single stacking faults result in twinned crystals. A new twin relation (180° rotation about the [100] axis) has been recognized. Twenty specimens from extreme geological environments have been examined in order to evaluate the control of environment on the stacking. The type of stacking could not be attributed solely to the influence of pressure and temperature. Composition appears to play a dominant role in the type of stacking, and semi-quantitative structural arguments appear to support this contention. The influence of growth mechanism is discussed. A scheme for the identification of the mica polymorphs by X-ray powder and single-crystal methods is given.

IN the course of an experimental investigation of the stability ranges and relations of phlogopite and muscovite by Yoder and Eugster (1954, 1955), it was found difficult to identify some mica polymorphs from X-ray powder patterns and it was necessary to establish a standard X-ray powder pattern for each polymorph. Although a large number of specimens had been examined in the past, especially in the extensive study of Hendricks and Jefferson (1939), it was not certain that all possible polymorphs had been discovered. For these reasons it was desirable to develop a theory which would permit the prediction of all the possible polymorphs. This theoretical study led to an examination

of the factors which govern the growth of the polymorphs. An understanding of these factors required study of the growth mechanism and twin laws as well as of the effect of the environment and the crystal structure. Since the polymorphs could not all be synthesized by Yoder and Eugster it was necessary to augment the synthetic studies by the identification of polymorphs obtained from a wide range of geological conditions. In the absence of detailed crystal-structure data an evaluation of the structural controls from semi-quantitative considerations was required.

Possible polymorphs.

The structure of a mica polymorph was first established by Jackson and West (1930, 1933) for a 2-layer monoclinic muscovite. Hendricks and Jefferson (1939) demonstrated the existence of other polymorphs and determined their structures. They showed that all the polymorphs were based on the same sub-cell. Polymorphism in the micas occurs because the atomic arrangement in the sub-cell has monoclinic symmetry, whereas the symmetry of the surface of the sub-cell is hexagonal or pseudo-hexagonal. Rotation of a sub-cell by 60° does not affect the packing of the surfaces but does affect the position of the sub-cell.

The features of the mica structure important to this study are given in fig. 1*a*, *b*, *c*. A more complete set of diagrams of the mica structure may be found in the 'Atomic Structure of Minerals' by W. L. Bragg (1937, pp. 205 ff.). All ions in the mica structure are in parallel pseudo-hexagonal arrays. In each mica layer there are two sheets of oxygen tetrahedra containing silicon and aluminium. Each sheet consists of tetrahedra linked at each of three corners to form an hexagonal array with all the bases parallel and all the vertices pointing the same way. The two silicon-aluminium sheets that are contained in each mica layer are parallel and have opposing vertices. They are held together by Mg or other ions in octahedral coordination. For convenience, the basal oxygen ions of the Si and Al tetrahedra will be denoted O_B and the oxygen atoms at the apices, O_A (see fig. 1*b*). The O_A atoms form an hexagonal array and the centres of the array are filled by OH or F ions (fig. 1*a*). Each Mg ion is linked to $2O_A + 1OH$ from the upper silicon-aluminium sheet and $2O_A + 1OH$ from the lower sheet. Although all atoms are in hexagonal arrays, the linkage at the Mg ions reduces the layer symmetry to monoclinic with a layer stagger of $1.7 \text{ \AA}$. Each layer has a vertical plane of symmetry passing through the OH ions (fig. 1*a*), and the layer is face centred, giving a symmetry of *Cm*. The layers are linked by K

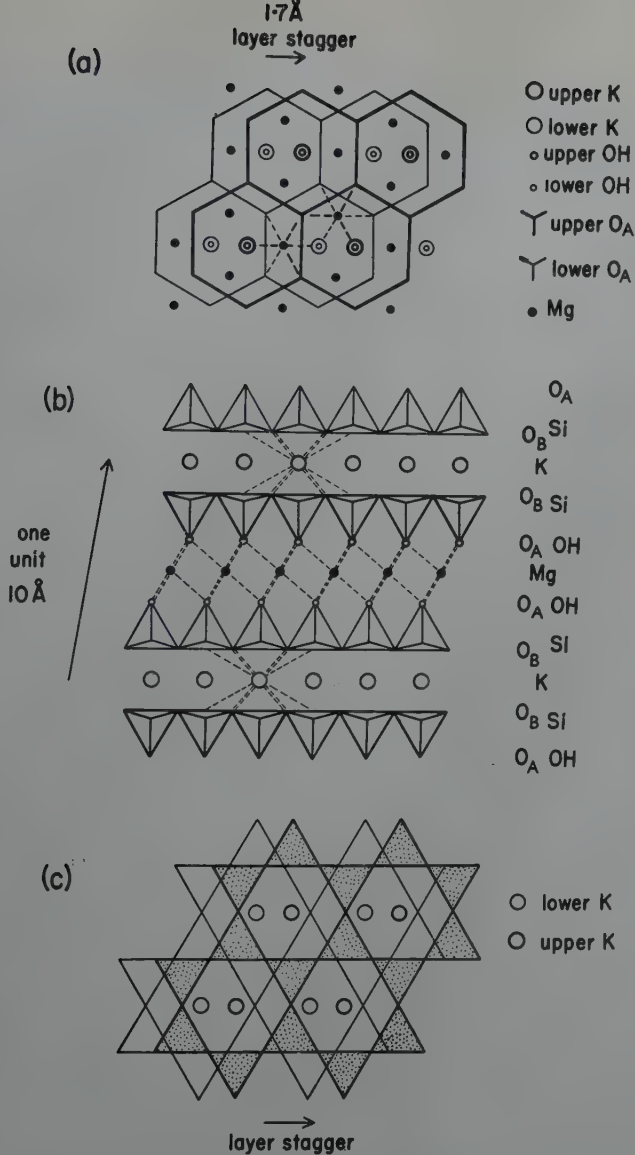


FIG. 1. (a) A projection normal to one mica layer showing the K (○), Mg (●), and OH (○) ions. The O_A oxygen atoms are at the corners of the hexagons. The thick and thin lines and circles in this figure and in fig. (c) represent the upper and lower layers of atoms in the unit. (b) A projection on (010) showing one layer together with the adjacent parts of the two adjoining layers. The O_A oxygen atoms overlap with the OH ions. The O_A and O_B oxygen atoms are at the vertices of the tetrahedra. The K, Si, Mg, and OH ions may be replaced by other ions. (c) A projection normal to one mica layer showing only the K (○) and O_B atoms. The O_B atoms are at the corners of the hexagons.

ions in 12-fold coordination (six O_B atoms from each layer). The O_B atoms form two hexagonal arrays and each K ion sits symmetrically in the centre of an hexagonal prism. The O_B atoms above and below the K ions superpose exactly, giving no layer stagger at the interface (fig. 1b).

The different ways of stacking two adjacent mica layers will now be enumerated. As the layer stagger is equal to the horizontal displacement of either the O_B atoms or the K atoms and the interlayer stacking is concerned only with these atoms, it is only necessary to consider these atoms for the present purpose. When a new layer is added to the top of the first layer, the six lower O_B atoms of the new layer superpose directly on the six upper O_B atoms of the first layer. Because of the hexagonal symmetry of these oxygen sheets there are six possible orientations of the new layer which are related by 60° rotations. Correspondingly, the directions of stagger of the two layers may be at any one of the six angles 0° , 60° , 120° , 180° , 240° , and 300° . Because of the plane of symmetry of the layer that is parallel to the layer stagger, angles 60° and 300° are equivalent, as also are angles 120° and 240° . There are, therefore, four different ways of stacking two adjacent layers. The simplest way of depicting the stacking sequence is to show the positions of the K atoms on a projection taken normal to the mica layer. It is convenient to draw vectors from one K atom to a K atom in the next layer with the arrowhead showing the direction of increasing height of the mica layers (see fig. 2).¹ From the positions of the K atoms the positions of the other atoms may be reconstructed. The angle between two interlayer vectors, the *interlayer stacking angle*, is measured in the counterclockwise direction in this paper.

If there is no control over the choice of the interlayer stacking angle, disordered crystals will result, whose stacking angles occur in random sequence. Each layer will have its atoms in fixed positions: this is random stacking of *whole layers*, not of *individual atoms*. Different sorts of disordered crystals may be obtained by restricting the possible stacking angles. For example, two extreme types of disordered crystals can be built; one containing a random mixture of 0° , 120° , and 240° stacking angles, and the other containing a random mixture of 60° , 180° , and 300° stacking angles.

If there is complete control over the layer stacking, fully ordered crystals will result. By taking all combinations of the stacking methods,

¹ Ramsdell (1947) has used a similar method for describing the polymorphs of SiC, and Dekeyser and Amelinckx (1953) have used this method for describing the mica structures.

an infinity of structures may be constructed. However, it may be expected that, if layers start growing with a particular stacking angle,

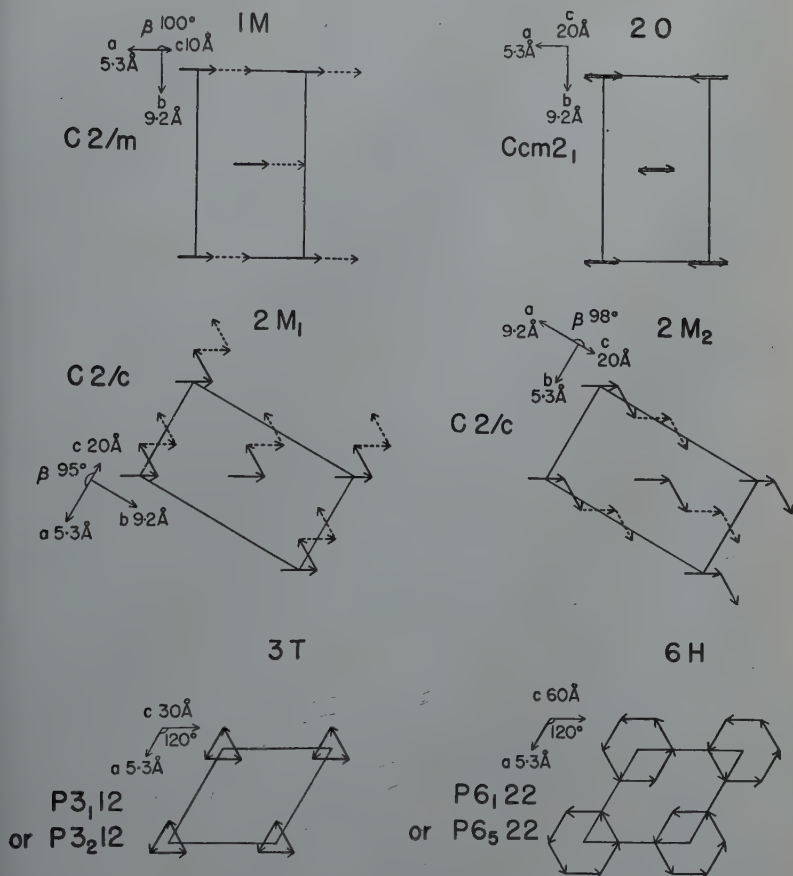


FIG. 2. The six simple ways of stacking mica layers in an ordered manner. The arrows are the interlayer stacking vectors. Full line vectors show the layer stacking in one unit cell, whereas the broken line vectors show the positions of layers in the next unit cell. The base of the unit cell is shown by thin lines, and the space group and lattice parameters are listed by the side of the diagram. Note that there are two possible directions of screw of the stacking vectors in the 3T and 6H polymorphs corresponding to the two space-groups listed for each polymorph. Pabst (1955) has recently shown that the ideal structure of a 1M mica has the space-group $C2/m$.

additional layers will also have this stacking angle. On the condition that only one stacking angle occurs, six polymorphs may be built as

shown in fig. 2. For convenience, a simple nomenclature has been adopted in which the first symbol gives the number of layers in the repeat unit and the second gives the symmetry. The polymorphs are 1M, 2M₁, 2M₂, 2O, 3T, and 6H. As there are two 2-layer monoclinic (2M) polymorphs, the subscripts 1 and 2 are used. The letter O represents orthorhombic; T, trigonal; and H, hexagonal. The derivation of the six simple polymorphs is as follows. The only polymorph that can be built solely from the 0° stacking angle is the 1M structure. Similarly the 2O structure is the only one that can be built solely from 180° stacking angles. If 120° and 240° stacking angles are used, three simple arrangements can be found, two of which are merely mirror images. They are: a continuous sequence of 120° angles; a continuous sequence of 240° angles, which gives rise to a mirror image of the 120° sequence; and a continuous alternation of 120° and 240° angles. The first two give the 3T polymorph and its mirror image; the third gives the 2M₁ structure. The derivation of the polymorphs based on the 60° and 300° angles is identical. The three structures formed are: a continuous sequence of 60° angles; a continuous sequence of 300° angles, which gives rise to a mirror image of the 60° sequence; and a continuous alternation of 60° and 300° angles. The first two are the 6H polymorph and its mirror image and the remaining one is the 2M₂ polymorph. It should be noted that the 2M₁ and 2M₂ polymorphs have quite different stacking arrangements even though they belong to the same symmetry system and have the same repeat unit.

If only an occasional stacking fault—that is, a mistake in the repeated sequence of layers—occurs in ordered crystals, twinned crystals result, as described in a later section.

Observed polymorphs.

Mauguin (1927, 1928) showed that the *c*-axis of a biotite was apparently one-half that of a muscovite. Pauling (1930) proposed a structure for the micas, and Jackson and West (1930, 1933) independently established the structure of a muscovite (now called 2M₁). Hendricks and Jefferson (1939), in an important and extensive survey of about 100 micas, identified and gave detailed structures for six polymorphs, which may be denoted in the new nomenclature, 1M, 2M, 3T, 6M, 6Tc (triclinic or anorthic), and 24Tc. Axelrod and Grimaldi (1949) described a 3M muscovite, and Amelinckx and Dekeyser (1953) demonstrated the existence of an 18-layer monoclinic biotite. Levinson (1953), in a study of lepidolites, confirmed the existence of 1M, 2M, 3T, and 6M poly-

morphs. The 1M, 2M, and 3T¹ micas are identical with the theoretical polymorphs 1M, 2M₁, and 3T described in this paper.

Axelrod and Grimaldi (1949) described the first example of a 3-layer muscovite and they showed that the geometry of the sharp reflections was trigonal. They suggested, however, that it might be monoclinic because of the finite value of 2V and the asymmetry of the diffuse streaks observed in the Weissenberg photographs. This specimen (Sultan Basin) was re-examined, and it was found that the sharp reflections have intensities and interaxial angles corresponding to exact trigonal symmetry. The interaxial angles were measured on a precession camera with an accuracy of 5' of arc. The diffuse streaks were not asymmetric in intensity, and moreover they are caused by stacking faults in the crystal and do not reflect the symmetry of the ordered portions. There is, therefore, no evidence from the X-ray photographs that the symmetry of the ordered portions is other than trigonal. The finite values of 2V may be caused by strain or by some other factors. It is well known that the 'optical' symmetry can differ from the 'X-ray' symmetry, and this may be attributed to the difference of wave-length of the two radiations. Structural deviations of approximately the wave-length of X-rays will result in observable X-ray phase changes; whereas deviations much greater than these wave-lengths may result in uncorrelated and consequently unobservable phase changes. Therefore, deviations that affect light (wave-length ~ 6000 Å.) need not affect X-rays (wave-length ~ 1 Å.).

Examination of the 6M structure given in fig. 6c and table 10 of the paper of Hendricks and Jefferson (1939) shows that a smaller unit cell may be taken. This new unit cell is identical with that for the theoretical 2M₂ polymorph and one-third as large as the original 6M cell. That this new cell is not a pseudo-cell is shown both by the systematic absences recorded by Hendricks and Jefferson and by a new set of X-ray photographs of a specimen (Stevens, no. 7) described as having the 6M structure by Hendricks and Jefferson. All reflections could be indexed on the smaller unit cell. The 6M mica (found so far only in lepidolites) is therefore renamed 2M₂, for its true repeat is only two layers. The 6M cell has symmetry *Cc* with $a = 9.2$, $b = 5.3$, $c = 60$ Å., $\beta = 90^\circ$; the smaller 2M₂ cell has symmetry *C2/c* with $a = 9.2$, $b = 5.3$, $c = 20$ Å., and $\beta = 98^\circ$.

¹ Called rhombohedral by Hendricks and Jefferson and hexagonal by Levinson. The term trigonal is preferred in accordance with the 1952 edition of 'International Tables for X-ray Crystallography'.

The existence of the 6-layer triclinic structure described by Hendricks and Jefferson was not confirmed. X-ray examination of the biotite from Sterling Hill, N.J. (U.S.N.M. C3675), showed that it has a $2M_1$ structure, and not the 6Tc structure assigned by Hendricks and Jefferson. The X-ray photograph which Hendricks and Jefferson describe as a zero-layer, *a*-axis Weissenberg photograph (reproduced by them as fig. 4i) is identical with a zero-layer, [110]-axis Weissenberg photograph of a $2M_1$ crystal. By taking new *a*- and *b*-axes, the 6Tc unit cell may be transformed into a $2M_1$ unit cell. It is concluded, therefore, that the 6Tc structure is a $2M_1$ structure described on different axes.

Re-examination of the 24-layer triclinic mica described by Hendricks and Jefferson (biotite, U.S.N.M. 34476) confirmed the triclinic symmetry. Weissenberg photographs about all three of the 5.3 Å. axes, however, could be indexed on an 8-layer unit cell, and could not be interpreted as twinning of a crystal containing a smaller number of layers. This 8Tc polymorph is not included in the list of the 'simple' polymorphs deduced from the theoretical study and it must have, therefore, a complex stacking scheme.

From Laue photographs Amelinckx and Dekeyser (1953) have demonstrated the coexistence in a biotite crystal from Monte Somma of a 1-layer monoclinic portion with another monoclinic part consisting of some 18 layers (the exact number of layers is difficult to determine when the number is so large, for indexing is uncertain).

A crystal of 'ephesite' from Postmasburg, South Africa, kindly supplied by Dr. W. T. Schaller, was examined by Weissenberg methods, which revealed the existence of a further polymorph. The symmetry is monoclinic and the strong reflections agree closely, both in position and in intensity, with those from a $2M_1$ polymorph. Weak reflections at distances corresponding to one-third of the separation of the strong reflections indicate that the repeat unit is at least 6 layers; in addition, very faint reflections appear approximately midway between the weak reflections. Although the reflections are so weak that it is difficult to be sure that they lie exactly at the midway points, the unit cell probably consists of 12 layers.

Disordered polymorphs have been observed by Hendricks and Jefferson in natural materials and by Yoder and Eugster (1954, 1955) in synthetic micas. Hendricks and Jefferson, as well as Yoder and Eugster, have described all variations from ordered to disordered polymorphs. The partially disordered materials contain a large number of stacking faults, the percentage of faults increasing with disorder until

finally the stacking is random. The effect on the X-ray pattern is explained by Hendricks and Jefferson in the following way:

Inspection of the various drawings and tables of coordinations will perhaps make it evident that translation of one-half of a mica layer by $nb/3$ with respect to the other half leaves the layer unchanged but results in a change of relationship of successive layers. This is really the factor which permits the polymorphism of the octophyllite micas. Now if this process is carried out in a random instead of a regular manner there will be no definite c periodicity unless the k index is a multiple of three, in which case the periodicity is that of a single layer. As a result diffuse scattering of the observed type will necessarily appear, and its intensity will depend on the number of the random shifts.

It is thus found that of the simple polymorphs only the 2O and 6H polymorphs have not been found so far in nature. The other four simple ordered polymorphs 1M, $2M_1$, $2M_2$, and 3T and the disordered polymorphs are found in nature. If the 6H polymorph does occur in nature it probably occurs in the lepidolite group, since this is the only mica group to produce the $2M_2$ polymorph, whose stacking is related to that of the 6H polymorph. In addition to the four simple ordered polymorphs, three more ordered polymorphs have been identified: 12M, 18M, and 8Tc. These polymorphs occur only very rarely in nature, probably under conditions that favour the operation of the spiral-growth mechanism. The great majority of the micas fall into the four structural types 1M, $2M_1$, $2M_2$, and 3T, whose structures consist of the simplest stacking of mica layers. The structures of the 8Tc and 12M micas must be closely similar to those of the $2M_1$ polymorphs in view of the similarities between the X-ray patterns that have been found. Only with much effort would it be possible to determine the exact structure of these complicated polymorphs, for the number of possible polymorphs containing a certain layer periodicity increases very rapidly with the number of layers. It is possible that other factors operate besides interlayer stacking; for example, two polymorphs may have the same layer stacking but different distribution of the ions in the layers. Only very detailed intensity calculations would permit evaluation of such factors.

Twinning.

Frequent random stacking faults result in disordered crystals; the occurrence of a single stacking fault in an ordered block of crystal gives rise to a twinned crystal. The possible twin laws may be enumerated by introducing all the possible stacking faults into an

ordered structure, using a vector diagram. A complete list need not be given here.

Twinning on a $[310]$ axis, with composition plane (001) , has been known for a long while and is referred to as the common mica twin law. A search of the literature reveals that this type of twin law has been found in all the common micas. This suggests that the same twin law operates for several polymorphs, although careful determinations of both the twin law and the type of stacking for a series of specimens would be needed before this could be definitely established.

The introduction of a single mistake in the stacking of a $2M_1$ polymorph may lead to twinning about the $[310]$ axis in two ways (fig. 3a, b, c). The interlayer stacking vectors of a $2M_1$ structure bear alternately an angular relation of 240° and 120° (the angular rotation is taken counterclockwise throughout this paper). If a single fault occurs in which the 240° angular relation replaces a 120° angular relation (fig. 3b), a twin about the $[310]$ axis results (fig. 3a). In detail, the sequence of angles in fig. 3b is $120^\circ, 240^\circ, 120^\circ, 240^\circ, 120^\circ, 120^\circ$ (fault), $120^\circ, 240^\circ, 120^\circ, 240^\circ$. If a single fault occurs in which a 0° angular relation replaces a 120° angular relation (fig. 3c), a twin about the $[310]$ axis also results (fig. 3a). Similarly, in fig. 3d, e, f the introduction of a single mistake may lead to a twin about the $[3\bar{1}0]$ axis. In fig. 3e a 240° angle replaces a 120° angle, and in fig. 3f a 0° angle replaces a 240° angle; the stereogram for the $[3\bar{1}0]$ -axis twin is given in fig. 3d. For a 1M polymorph (fig. 3g, h) a stacking error of 240° again leads to the same twin law; this stacking error involves replacement of one of the 0° angles by either a 120° or a 240° angle. It may be shown that a displacement of the upper half of a layer by $nb/3$ with respect to the lower half is equivalent to a change of 120° in the interlayer stacking angle. A displacement of $nb/3$, therefore, would lead to twinning about the $[310]$ axis in a 1M or $2M_1$ polymorph. (It is interesting to note that the fault in a $[310]$ twin axis of a 1M, a $2M_1$, or a 3T polymorph is used in one of the other polymorphs as a stacking element.)

This type of twinning was found in a 1M crystal of phlogopite from Chester, Vermont. A zero-layer, a -axis Weissenberg photograph contained reflections lying near the positions of reflections from a 3T polymorph; the anomalous intensity distribution, however, indicated that this specimen of phlogopite has a 1M structure and is twinned about both the $[310]$ and $[3\bar{1}0]$ axes. The spots on the photographs, instead of lying on smooth curves with a uniform variation of intensity, lie on a slight zigzag with every third reflection staggered in the same direction

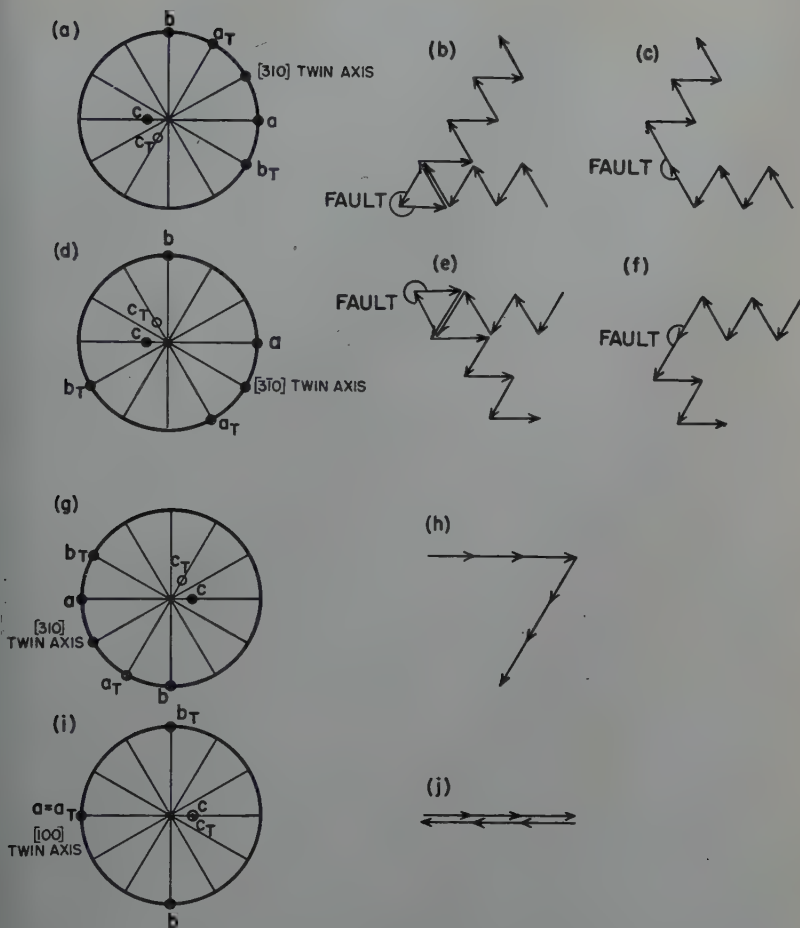


FIG. 3. (a) and (d) are stereograms showing the angular relations between the two twin components and (b), (c), (e), and (f) show the stackings which lead to the twinning of a $2M_1$ structure on the $[310]$ and $[\bar{3}\bar{1}0]$ axes. Notice that replacement of a 120° by a 240° or a 0° stacking angle leads to the same twin law but by a different method. Both (b) and (c) give the angular relation in stereogram (a); similarly with stereogram (d) and stacking diagrams (e) and (f). Stereogram (g) and stacking diagram (h) show the twinning of a 1M structure about the $[310]$ axis. Stereogram (i) and stacking diagram (j) show the twinning of a 1M structure about the $[100]$ axis.

and having the same intensity anomaly. Other crystals from the same hand specimen contained an untwinned 1M structure and still others the 3T structure.

Examination by Weissenberg methods of a mahadevite crystal from Racha Konda, India, contributed by Professor C. Mahadevan, has revealed the occurrence of a new twin law. The crystal has a 1M structure and is twinned about the [100] axis with (001) as the composition plane. The crystals were not suitable for an examination of the surface morphology and the twin law could not be confirmed from the morphology. This type of twinning can be explained (fig. 3*i*, *j*) by postulating the existence of a 180° stacking angle in the ordered sequence of 0° angles that forms the 1M type of structure. This type of twinning is related to the theoretical 2O polymorph, which is built solely from 180° stacking angles.

Factors governing the growth of polymorphs.

If the stacking of the layers in the mica structure were uncontrolled, completely disordered structures should always result. In the majority of the natural and synthetic specimens examined so far, the structure is reasonably well ordered, thus demonstrating the existence of controlling bond forces. The presence of stacking disorder, either partial or complete, in some of the micas shows that the controlling bond forces may be weak and may be rendered inactive under some thermodynamic conditions. In this section an attempt is made to evaluate the relative dominance of the various structural factors which control the stacking of the mica layers.

Observations on the mechanics of growth contribute to an understanding of the structural controls. Two mechanisms of growth have been recognized: growth of perfect crystals by secondary nucleation of each individual layer (Kossel, 1927; Stranski, 1928; Stranski and Kaischew, 1931); and growth of imperfect crystals (Burton, Cabrera, and Frank, 1949) by propagation of one nucleus into many layers of identical structure by spiral growth arising from a dislocation (cf. Frank, 1952). Several workers have examined the surface topology of micas by the method of multiple-beam interferometry developed by Tolansky. Tolansky (1945, 1946*a*, 1946*b*) showed that the surface of a mica sheet is violently contorted and crossed by cleavage steps, the heights of which appeared to be multiples of the *c*-spacing. According to Courtney-Pratt (1950), these cleavage steps were multiples of 10 Å. It was also shown by Tolansky that micas can be cleaved true to a single layer over large areas of many square centimetres. Tolansky and Morris (1947) investigated the surface topology of cleaved natural micas by an interferometric method which measures the thickness of the sheets. They

found that muscovites exhibited large areas of uniform thickness which contain very few inclusions; the average size of the uniform areas was 1 sq. cm. and the number of inclusions was about 10 per sq. cm. The phlogopites and biotites exhibited only small areas of uniform thickness and contained many inclusions, about 100 per sq. cm. The absence of spirals is consistent with either secondary nucleation of perfect crystals or spiral growth with the original dislocations having extended themselves over all the examined faces of the crystal so that they can no longer be detected. Amelinckx (1952) and Amelinckx and Dekeyser (1953) have demonstrated that cleavage faces of muscovite contain emerging screw dislocations and that growth spirals occur on a biotite crystal. It appears certain, therefore, that at least some micas have grown by the dislocation mechanism of Frank. The other micas may have grown by either method. It should be noted that these experimental observations apply only to large, well-developed crystals suitable for use in a multiple-beam interferometer. Fine-grained micas have not been examined in this apparatus and may have quite different surface topologies.

If growth proceeds by secondary nucleation of each additional layer there is no necessity for the added layers to adopt a fixed orientation unless other factors control the orientation. However, if growth proceeds by the spiral mechanism, the added layers must adopt the orientation of the primary nucleus and the resultant crystal will consist of a single ordered type of stacking. The type of stacking will thus be governed by the structural bond forces of the primary nucleus.

The second consideration involves the nature of the mica structure itself, and some of its properties will now be examined for evidence of specific structural bond controls. The pseudo-hexagonal stacking of the atoms in the mica structure results in weak structural control between adjacent sheets. The larger the deviation from hexagonal symmetry of the sheets of atoms, the larger will be the structural bond forces that control the orientation of adjacent layers. It should be noted, however, that even if all the atoms lie in arrays whose symmetry is exactly hexagonal there should still be a small controlling bond force, for the hexagonal sheets of atoms in any one layer are arranged in such a way as to give monoclinic symmetry. This bond force is probably quite small, for it arises in the stagger of the two halves of the mica layer that adhere at the octahedrally coordinated ions and it must operate through hexagonal arrays of SiO_4 and AlO_4 tetrahedra, which act as an electrostatic screen. In addition, asymmetry will arise from the

distribution of Si and Al atoms in the tetrahedral sheet unless the Si and Al atoms are disordered.

Unfortunately, accurate structure determinations of the micas have not yet been made, and it is necessary to use qualitative arguments to evaluate the nature of the structural bond forces. As mentioned by Hendricks and Jefferson (1939), the $(06l)$ reflections with l odd have zero intensity if all the ions occupy the ideal sites of hexagonal arrays. Muscovite and other dioctahedral micas give fairly large intensities for these reflections, showing that there is considerable deviation from the ideal structure. As shown by Jackson and West (1930), the observed angle β for a $2M_1$ muscovite is $95^\circ 30'$, which deviates considerably from the value of $94^\circ 55'$ calculated for an ideal structure. Similarly the angle β for a $1M$ muscovite is $101^\circ 35'$ (Yoder and Eugster, 1955) instead of the ideal value of $99^\circ 41'$. For natural $1M$ phlogopites, however, measurements of β with a precession camera have agreed within the experimental error of $5'$ with the ideal value of $99^\circ 49'$. The lengths of the a - and b -axes should be controlled dominantly by the linked array of SiO_4 and AlO_4 tetrahedra, for these provide the strongest linkages in the micas. Using the value $1.645 \pm 0.01 \text{ \AA.}$ for the distance Si_3Al_3-O (Smith,

TABLE I. Measurement of b ($\text{\AA.}$) for muscovite and phlogopite polymorphs.

	Muscovite.	Phlogopite.
Natural $1M$	—	9.20^*
Synthetic $1M$	$9.00^\dagger$	$9.20^\ddagger$ (or $3T$)
Natural $2M_2$	9.02^*	$9.23^\ddagger$
Synthetic $2M_2$	$9.00^\dagger$	—
Natural $3T$	$9.01^\dagger$	9.21^*

* Present work.

† Yoder and Eugster (1955).

‡ Yoder and Eugster (1954).

1954) and assuming an ideal parallel array, b should equal $9.30 \pm 0.06 \text{ \AA.}$ and $a = b/\sqrt{3}$. Both muscovite and phlogopite satisfy the condition $a = b/\sqrt{3}$. The measurements of b for the muscovite and phlogopite polymorphs are given in table I. The values for phlogopite fit quite well with the ideal value, thus suggesting that the tetrahedra are in closely parallel arrays. The values for muscovite, however, are 3 % smaller than the ideal value, suggesting that the sheets of tetrahedra are buckled. It is plausible to suppose that in muscovite the sheets of tetrahedra collapse about the vacant octahedral sites. It is concluded from this evidence that there is considerable bond control over the stacking of dioctahedral micas and a smaller bond control over the stacking of trioctahedral micas.

In addition to the evidence provided by observations of the mechanics of growth and the properties of the mica structure itself, observations obtained on the synthesis of micas by Yoder and Eugster (1954, 1955) contribute to the problem of the nature of the controlling bond forces. They found that at high temperatures, hydrothermal growth of synthetic mica is relatively rapid and equilibrium can be demonstrated. Synthetic muscovite (which may be taken as a typical example of a dioctahedral mica) crystallizes with the $2M_1$ structure; whereas phlogopite (a typical trioctahedral mica) crystallizes with the 1M, 3T, or both 1M and 3T structures (the identity of the powder patterns of 1M and 3T phlogopite precludes identification of the fine-grained synthetic crystals). Equilibrium at the high temperatures has been approached by converting a 1M and a 3T muscovite into a $2M_1$ muscovite, and a $2M_1$ phlogopite into a 1M, 3T, or both 1M and 3T phlogopite. These results are in agreement with those found by examination of natural micas from high-temperature environments. The muscovites from geologically high-temperature environments almost invariably have the $2M_1$ structure; whereas the phlogopites generally have the 1M structure, but occasionally the 3T and other structures. The trioctahedral biotite often has a wide variety of structures including very complex ones such as the 8Tc and 12M already mentioned. The larger size of natural crystals allows the use of single-crystal methods, and all workers who have used this technique agree that stacking disorder does not occur in $2M_1$ muscovites but is common in phlogopites and biotites—sometimes amounting to almost completely random stacking.

According to Yoder and Eugster, at low temperatures a different situation occurs with regard to the relative dominance of the polymorphs. In the laboratory, muscovite first crystallizes with the completely disordered structure (1Md), which changes into the 1M structure during longer runs or at higher temperatures. On raising the temperature the 1M structure can be converted into the $2M_1$ structure. The reactions are so sluggish that equilibrium cannot be demonstrated. It is possible that the 1M structure is stable at low temperatures and it is probable that the transformation 1Md to 1M depends on the reaction rate. At low temperatures phlogopite also grows with the 1Md structure, which transforms into the 1M, 3T, or both 1M and 3T structures in the course of time or at higher temperatures. It is again probable that this reaction depends on factors affecting the reaction rate. It is believed that in nature the progressive metamorphism of sediments leads to the transformation $1Md \rightarrow 1M \rightarrow 2M_1$ for muscovite in accordance with the

laboratory results. For phlogopite both 1Md (trioctahedral clay mica) and 1M structures have been found in low-temperature environments.

With this review of the experimental evidence, the relative merits of the hypotheses of growth by secondary nucleation and by the spiral mechanism, and the extent to which growth is controlled by structural factors, can now be examined:

If growth proceeds by secondary nucleation and there is no structural bond control, randomly stacked structures should result. If there is a little structural control, partially ordered crystals containing large regions of 1Md should occur.

If growth proceeds by the spiral mechanism and there is no structural bond control, ordered crystals should occur because the spiral mechanism provides a 'memory'. All polymorphs should occur in all possible environments since there is no structural control over the selection of the polymorph. It would be expected that the simpler ones would predominate, and that the order of abundance would be 1M; 2M₁, 2M₂, and 2O; 3T, 6H, &c.

If growth proceeds by secondary nucleation and there is complete structural control, ordered crystals should occur. Only one polymorph should occur for any one composition, temperature, and pressure. Different compositions could give different polymorphs and different polymorphs could be stable at different pressures and temperatures, for the crystal structure is a function of composition, pressure, and temperature. If the structural control is not complete, disorder can occur. This will not result in complex polymorphs, for the secondary nucleation growth mechanism has no 'memory'.

If growth proceeds by the spiral mechanism and there is complete structural control, the same result will occur as for growth by secondary nucleation with complete structural control. If the structural control is not complete, faults will occur sometimes and these will give complex polymorphs which retain their high repeat distances from the 'memory' of the spiral.

The growth of 1Md phlogopites and muscovites at low temperature fits most easily with the hypothesis of secondary nucleation and no structural control. The growth of 2M₁ muscovites at high temperature, with the absence of disorder and polymorphism, is explained by complete structural control and growth by either mechanism.

The growth of phlogopites and biotites at high temperatures, with the observed tendency to give 1M, 3T, or both 1M and 3T polymorphs, suggests a moderate structural control that can often be overwhelmed.

The presence of complex polymorphs, although rarely observed, definitely suggests operation of the spiral mechanism. The presence of random stacking disorder suggests that crystals containing this disorder grew by the method of secondary nucleation.

These two suggestions of complete control of the muscovites and moderate structural control of the phlogopites and biotites agree well with the semi-quantitative deductions concerning the distortion of the mica layers. It is highly desirable that accurate determinations of the atomic coordinates of these structures be carried out in order that the structural controls can be more fully evaluated. From these determinations it should be possible to determine why muscovite adopts the $2M_1$ structure and phlogopite and biotite tend to adopt the $1M$ structure.

Dekeyser and Amelinckx (1953) believe that the ions in the octahedral sites are not able to control the stacking of the mica layers, for they would have to influence the fourth nearest neighbours. It is the view of the present writers that the inferred distortion of the sheets of tetrahedra in the muscovite structure gives a direct linkage between the upper and lower surfaces of each mica layer, and hence the stacking is controlled without recourse to direct interaction between fourth neighbours. In trioctahedral micas there should be a small force arising from the monoclinic nature of each layer which requires interaction only between second neighbours.

Rejecting structural control (p. 26) Dekeyser and Amelinckx state in their English abstract that:

1. . . . The high frequency of polytypes in the trioctahedral types is correlated with growth conditions. For concision order and disorder are used in the sense of strict regularity resp. irregularity in the superposition of layers.

2. Order of micas and related clay minerals results from growth following the *mechanism of Frank*, as exemplified by the biotite considered in Part 1. This means growth at low supersaturations. Disorder occurs when growth proceeds by secondary nucleation.

3. Partial order means that the crystal has developed through different stages of supersaturation. Such crystals must generally be considered formed by the juxtaposition of a disordered part and one or more highly ordered ones.

4. The high percentage of order present in dioctahedral clay minerals (when their dimensions are superior to those of the primary nuclei) and the absence of polytypes indicates formation in conditions chemically not too complex, and at low supersaturation.

5. High degree of disorder, frequent polytypism, characteristic for trioctahedral minerals (with same restrictions as above) are the result of growth at higher temperatures and (or) complex chemical environment. In fact these conditions seem to be only compatible with the dioctahedral¹ type.

[¹ Misprint for trioctahedral?]

While it is agreed that disorder can occur when growth proceeds by secondary nucleation, it does not follow that order must always result from growth following the mechanism of Frank. It is considered by the writers that order may also result from growth by secondary nucleation if the structural control is strong. Furthermore, partial order may result either from development through different stages of supersaturation or from growth in which the structural control is only moderate so that the structural control may sometimes be overwhelmed by environmental conditions. Under the second hypothesis it is not necessary to consider that partially ordered crystals must be formed of the juxtaposition of a disordered part with one or more ordered ones; the ordered and disordered regions may be so intermixed that no separation of blocks can be made. The high order of dioctahedral micas formed *at high temperatures* results from strong structural control and not from the supersaturation. As cited above the dioctahedral micas contain considerable disorder when grown at low temperatures. The high degree of disorder and frequent polymorphism result from the presence of only moderate structural control. Since partially ordered phlogopites and biotites occur in the same hand specimen as fully ordered muscovites, it is clear that temperature does not have the dominant role ascribed by Dekeyser and Amelinckx.

It should be obvious from the frequent resort to qualitative and semi-quantitative evidence in the arguments presented in this section that much additional work is needed in order to resolve fully the issues discussed here. Further studies by interferometric and X-ray methods (such as those carried out by Amelinckx and Dekeyser, 1953) on crystals from a wide range of geological environments should be made. Detailed study of the ionic distribution in the mica structures is needed in order that accurate estimates of the structural forces can be made. Combination of the data from the two methods should result in more quantitative conclusions.

Polymorphism in natural micas.

In order to test the semi-quantitative deductions presented in the previous section, single crystals were selected from geological occurrences believed to represent a wide range of environmental conditions. They were obtained from intrusive and extrusive igneous rocks, low- and high-grade metamorphic rocks, alteration and contact zones, veins and pegmatites, and sediments.

Extrusive. Two specimens were examined from extrusive rocks.

Biotite 49-34 was collected by Dr. O. F. Tuttle at Camp Hale, Eagle Co., Colorado, from a flow rhyolite containing phenocrysts of biotite and quartz, the latter showing high-temperature morphology and inversion characteristics (Keith and Tuttle, 1952); the feldspars in the ground-mass were also indicative of high temperatures. Biotite B399 is from a flow rock in the Leucite Hills, Wyoming (Kemp, 1897); the specimen was collected by Dr. J. F. Kemp and contributed by Dr. Arie Poldervaart from the Columbia University collection. Both specimens gave a 1M structure, and it is for this reason that the synthetic phlogopite made at high temperatures (Yoder and Eugster, 1954) is believed to be 1M rather than 3T.

Intrusive. The biotite F2-183 from the Beinn an Dubhaich granite of the Isle of Skye was selected because the rock has the textural and compositional features of a granite, but with mineralogical features attributed to the rhyolites; it is considered by Tuttle and Keith (1954) to be a link between granites and rhyolites. One crystal was examined and found to have a 1M structure. Studies by X-ray powder diffraction of biotites and muscovites from a collection of common granites gave in all cases the 1M and $2M_1$ structures, respectively. For those granites that formed from a liquid, it has been shown that biotite is one of the first phases to appear. On the other hand, the appearance of muscovite in granites may be primary or secondary, depending on the pressure and temperature (Yoder and Eugster, 1954, 1955).

Pegmatites. The pegmatites yield the greatest variety of mica polymorphs, 1M, $2M_1$, $2M_2$, 3T, 8Tc, and larger units, as well as mixed-layer types. The phlogopites from the Burgess, Ontario, mica deposit gave, for example, 1M and $2M_1$ (U.S.N.M. 82459 and U.S.N.M. C3679, 1M; U.S.N.M. 106758, $2M_1$). Hendricks and Jefferson (1939, p. 765) cite the Ambulawa, Ceylon, pegmatite as one containing the $2M_1$, $2M_2$, and 8Tc polymorphs. The mahadevite specimen, (1M), a gift of Professor C. Mahadevan, is now considered, on the basis of the published analyses, to be close to eastonite in composition and does not lie midway between muscovite and phlogopite; it is described as occurring in a 'pegmatite vein which cuts through a band of micaceous schists in the khondalites (sillimanite garnet gneiss)' (Ramaseshan, 1945). The lepidolite ($2M_2$) from the Brown Derby Claim at Ohio City, Colorado (Stevens, 1938, U.S.N.M. 97893), was examined mainly because of its importance as an end member of what Levinson (1953) stated to be a complete series between lepidolite and muscovite. Levinson found that those micas having bulk compositions in the middle of the range actually had mixed-

layer structures of muscovite ($2M_1$) and lepidolite ($2M_2$) in contradiction to his concept of a complete series of solid solutions between muscovite and lepidolite. It is impossible for different structural types (e.g. $2M_1$ and $2M_2$) to form a complete series of solid solutions since it is not possible to turn one mica structure into another by a continuous displacive¹ transformation, but only by a reconstructive transformation.

Replacement. An example of a selective replacement mica is the Sultan Basin, Washington, muscovite collected by Dr. A. C. Waters and contributed by Mr. J. M. Axelrod (Axelrod and Grimaldi, 1949). According to Waters, the muscovite occurs as veinlets and replacements in granodiorite, and he visualizes the mica as forming from hot gases following the sheeting in the granite rock. The structure was found to be $3T$. Another example of a replacement mica is from Postmasburg, South Africa, where it was formed in argillaceous sediments along with the manganese ore minerals. The occurrence is described by Hall (1927) and the crystals by Phillips (1931). The mica was described as an ephesite (soda-margarite), but it may also be described as a lithium paragonite for the analysis shows large amounts of lithium. It is of special importance because it is the first mica high in soda that has been found in crystals suitable for single-crystal study. The one crystal examined was mainly $2M_1$, but gave indication of the presence of a $12M$ polymorph.

Contact. Two specimens described as having grown in contact zones were also studied. Palache (1935, p. 116) described a biotite (U.S.N.M. C3675) in the skarn zones where pegmatites cut the limestones at the Sterling Hill, New Jersey, zinc deposits and he thought that the mica would best be described as a manganophyllite. The mica from the Wissahickon schist near its contact with Baltimore gneiss near Germantown, Pennsylvania, is noteworthy for its low $2V$ and is described in detail by Postel and Adelhelm (1944). Both specimens have the $2M_1$ structure.

Hydrothermal alteration. One specimen representing growth by hydrothermal alteration also gave a $2M_1$ structure. It is a muscovite formed at the expense of a topaz crystal (U.S.N.M. 45075) from Stoneham, Maine, and classed with the rather ill-defined variety damourite (Clarke and Chatard, 1884).

Metamorphic. Micas from both high- and low-grade metamorphic rocks were examined. The muscovite (C-16) from the sillimanite zone

¹ A transformation in which atoms are merely displaced, in contrast to a reconstructive transformation, in which the structure breaks down and is rebuilt (M. J. Buerger, *Amer. Min.*, 1948, vol. 33, p. 101 [M.A. 10-380]).

(Barrow, 1912) in Glen Clova, Scotland, was found to have a $2M_1$ structure. The phlogopite (149) in a tremolite marble near Chester, Vermont, exhibited both the 1M and 3T polymorphs. A very large collection of biotites and muscovites from an area in which all grades of metamorphism may be found was examined by Dr. Vernon J. Hurst (unpublished, 1954) using powder X-ray diffraction techniques. The results indicated that all the biotites were 1M or 3T and all the muscovites were $2M_1$.

Sedimentary (?). Only one example of a mica believed to have grown diagenetically in a sediment and of a size suitable for single-crystal study was obtained. Carr, Grimshaw, and Roberts (1953) described a mica from a Yorkshire fireclay as a hydrous mica or an illite. Their published X-ray powder pattern was noted by them to be a mixture of mica and kaolinite. The presence of kaolinite would account for the excess water and low potassium obtained in the chemical analyses. The single-crystal study, as well as close examination of their X-ray powder pattern, indicates that the mica has a $2M_1$ structure. Although materials called illite and hydrous mica may contain micas having any structure or may even be mixtures, only that portion of the micas having a 1Md or a 1M structure is believed by Yoder and Eugster (1954) to be indicative of a low-temperature environment. One might suspect, therefore, that the $2M_1$ mica in the Yorkshire fireclay is of detrital origin and did not grow in the sediment.

It is concluded from these data on natural micas that there are factors other than environmental that determine the type of polymorph. Composition clearly has a strong influence on the structure. Aside from the obvious structural preferences of the common dioctahedral and trioctahedral micas, muscovite and biotite, respectively, there are compositional preferences within each of these groups, as exemplified by the limited solid solution between muscovite and lepidolite. Ordering forces are evident in the natural micas, particularly in the low-grade environments. The variation of structure in the natural micas cannot, therefore, be attributed solely to changes in pressure and temperature.

Identification of the mica polymorphs.

The structures of the mica polymorphs have many elements in common, resulting in difficulties in identifying the mica polymorphs from X-ray patterns. A rapid X-ray method of identification consists of taking a powder record either by photographic means or by the use of a Geiger counter focusing diffractometer. However, the dominant basal

cleavage results in preferred orientation, which is especially serious for the focusing diffractometers, and some care is needed in order to obtain satisfactory powder records. A more serious objection to the powder method is that 1M and 3T phlogopites (or other trioctahedral micas) give powder patterns that are indistinguishable (see below) and these polymorphs can only be distinguished by the use of single-crystal methods. The other common polymorphs, dioctahedral 1M and 3T, and the $2M_1$ and $2M_2$ polymorphs, however, can be identified from their powder patterns. It is doubtful whether the complex polymorphs such as the 12M can be identified by powder methods, for the strong reflections are similar to those for one of the simple polymorphs and the weak reflections are liable to be obscured in powder patterns. Table II

TABLE II. Data for identification of mica polymorphs from powder patterns; see also Levinson (1953). d in Å.

1M		$2M_1$		3T		1M and 3T		$2M_1$	
muscovite.†		muscovite.†		muscovite.†		phlogopite.‡		phlogopite.§	
<i>I.</i>	<i>d.</i>	<i>I.</i>	<i>d.</i>	<i>I.</i>	<i>d.</i>	<i>I.</i>	<i>d.</i>	<i>I.</i>	<i>d.</i>
vs	10.08*	vs	10.04*	vs	9.99*	vs	10.05*	vs	10.13*
w	5.04*	m	5.02*	s	4.99*	w	5.02*	w	5.06*
s	4.49	m	4.48	w	4.49	vw	4.59	w	4.61
		m	4.46	w	4.46	vw	4.55	vvw	4.52
w	4.35	vw	4.39						
		w	4.30						
vw	4.12	vw	4.11					vvw	4.08
		vw	3.97			vvw	3.93		
		w	3.89	w	3.87			w	3.81
m	3.66	w	3.74	w	3.60	vw	3.66		
		m	3.50			m	3.39	m	3.54
vs	3.36*	vs	3.35*	vs	3.33*	vs	3.35*	vs	3.36*
m	3.07	m	3.21	w	3.11	w	3.14	m	3.28
vvw	2.93	m	3.00			w	2.92	vvw	3.16
		w	2.87	w	2.88			s	3.04
		w	2.80			vw	2.71	vvw	2.93
vw	2.69	m	2.59	w	2.59	vw	2.64	w	2.82
m	2.58	m	2.58			m	2.62	w	2.65
s	2.56	s	2.56	m	2.56			vs	2.62
w	2.55	w	2.51*	vw	2.50*	m	2.51*	w	2.52*

* Basal reflections.

† Yoder and Eugster (1955).

‡ Present work, Table III.

§ Yoder and Eugster (1954).

contains the d values and intensities for the powder patterns of $2M_1$, 1M, and 3T polymorphs of muscovite, the identical patterns of 1M and

3T phlogopite polymorphs, and the $2M_1$ phlogopite polymorph. Data for the 1M, $2M_2$ (described as 6M by Levinson), and 3T polymorphs of lepidolite and the $2M_1$ of lithian muscovite have been given by Levinson (1953, p. 100, table 3). In his table 3, column 1, 3.20 should read 3.32, and in column 2, 4.94 should read 4.49. Muscovite and phlogopite may be taken as typical representatives of the dioctahedral and trioctahedral mica groups. In using table II for the identification of the polymorphs it should be realized that deviations of composition from the ideal muscovite and phlogopite formulae will result in small variations from the d values listed. As an example one may refer to the differences between a hydroxyl-bearing phlogopite and a fluorine-bearing phlogopite (Yoder and Eugster, 1954, pp. 170, 177). Preferred orientation in the powder specimen will give considerable variation in intensities from those listed in table II, for preferred orientation results in an increase of intensity for reflections whose planes are nearly parallel to (001) with a corresponding decrease for reflections whose planes are nearly normal to (001). The basal reflections (00 l) are starred in table II; these are enhanced most by preferred orientation.

The reason for the identity of the 1M and 3T phlogopite patterns is that the 1M and 3T polymorphs are based on the same sub-cell and that the 1M unit cell may be transformed into a cell with trigonal geometry. It can easily be shown that the 2θ values of the X-ray reflections are the same for the two polymorphs if: $a_M = a_T$; $b_M = b_T$; $3c_M \sin \beta_M = c_T$; $\cos \beta_M = -a_M/3c_M$ or $\cot \beta_M = -a_T/c_T$.

Since the structure of the sub-cell is ideally hexagonal for phlogopite, as revealed by (06 l) reflections, the intensities of the X-ray reflections will also be identical. Measurements of the lattice parameters of 1M and 3T natural phlogopites show that the geometrical conditions given above hold true within experimental error. In particular, the measured value of β_M agrees within the experimental error of about 5' of arc with the calculated value. In addition, the intensities of corresponding reflections measured from Weissenberg photographs are equal within experimental error for 1M and 3T phlogopite crystals.

Table III contains measurements of the powder patterns of a natural 1M and a natural 3T phlogopite together with the indices of the reflections. The agreement between the 2θ values and intensities is very close and the small differences in 2θ may be ascribed to small variations in the chemical composition. (A small amount of F replacing OH, for example, results in a large change in the c dimension without affecting the geometrical conditions governing the relation between the 1M and 3T unit

TABLE III. Powder records of 1M and 3T natural phlogopites. Cu- $K\alpha$ radiation.
 Intensities on an arbitrary scale.

1M			3T		
<i>I.</i>	$2\theta_{\text{obs.}}$	Indices.	<i>I.</i>	$2\theta_{\text{obs.}}$	Indices.
> 100	8.87	001	> 100	8.730	0003
6	17.67	002	23	17.660	0006
7	19.345	020	8	19.310	10 $\bar{1}$ 0
5	19.495	110	8	19.525	10 $\bar{1}$ 1
3	22.665	111	3	22.560	10 $\bar{1}$ 4
7	24.360	11 $\bar{2}$	7	24.300	10 $\bar{1}$ 5
20	26.3?	022	45	26.255	10 $\bar{1}$ 6
> 100	26.625	003	> 100	26.575	0009
10	28.385	112	25	28.350	10 $\bar{1}$ 7
7	30.655	11 $\bar{3}$	21	30.645	10 $\bar{1}$ 8
3	33.075	023	12	33.050	10 $\bar{1}$ 9
7	33.935	$\left\{ \begin{array}{l} 130 \\ 20\bar{1} \end{array} \right.$	10	33.910	11 $\bar{2}$ 1
30	34.305	$\left\{ \begin{array}{l} 200 \\ 13\bar{1} \end{array} \right.$	30	34.255	11 $\bar{2}$ 2
15	35.705	$\left\{ \begin{array}{l} 004 \\ 113 \\ 131 \\ 20\bar{2} \end{array} \right.$	52	35.730	$\left\{ \begin{array}{l} 0.0.0.12 \\ 1.0.\bar{1}.10 \\ 11\bar{2}4 \end{array} \right.$
15	36.985	$\left\{ \begin{array}{l} 13\bar{2} \\ 201 \end{array} \right.$	17	36.970	11 $\bar{2}$ 5
3	39.305	22 $\bar{1}$	3	39.245	20 $\bar{2}$ 1
?	39.8	$\left\{ \begin{array}{l} 220 \\ 132 \\ 20\bar{3} \end{array} \right.$	2	39.900	11 $\bar{2}$ 7
?	40.3	041	2	40.200	20 $\bar{2}$ 3
15	41.610	$\left\{ \begin{array}{l} 13\bar{3} \\ 202 \end{array} \right.$	21	41.590	11 $\bar{2}$ 8
30	45.05	005	> 100	45.090	0.0.0.15
7	45.47	$\left\{ \begin{array}{l} 204 \\ 133 \end{array} \right.$	12	45.450	1.1. $\bar{2}$.10
2	47.60	$\left\{ \begin{array}{l} 134 \\ 203 \end{array} \right.$	4	47.655	1.1. $\bar{2}$.11
?	52.335	$\left\{ \begin{array}{l} 20\bar{5} \\ 134 \end{array} \right.$	3	52.350	1.1. $\bar{2}$.13
15	54.825	$\left\{ \begin{array}{l} 13\bar{5} \\ 204 \end{array} \right.$	35	54.820	1.1. $\bar{2}$.14
15	60.285	060	25	60.235	30 $\bar{3}$ 0
2?	61.1	$\left\{ \begin{array}{l} 061 \\ 330 \end{array} \right.$	2?	61.12	30 $\bar{3}$ 3

cells.) The powder pattern of a synthetic phlogopite (given in Yoder and Eugster, 1954) can be indexed equally well on a 1M or a 3T unit cell.

On the other hand the 1M and 3T dioctahedral powder patterns (as exemplified by muscovite, table II) are not identical because the monoclinic unit cell cannot be transformed into a unit cell of the same shape as the trigonal cell. Measurements of β for a 1M muscovite differ by about $1^\circ 51'$ from the value required for geometrical equality. Furthermore, the intensities of corresponding reflections are not identical in accordance with the inferred distortion of the sub-cell.

As mentioned earlier, the 1M and 3T polymorphs may be readily identified from single-crystal moving-film photographs, but even with this method some care is needed; for example, a 1M crystal twinned on the $[310]$ and $[3\bar{1}0]$ axes gives a photograph similar to that of a 3T crystal.

Plates VIII and IX contain zero-layer $5.3 \text{ \AA}$. axis Weissenberg photographs of 1M and 3T crystals. There are three axes of $5.3 \text{ \AA}$. translation for each polymorph and only for the 3T polymorph are they identical. For the 1M polymorph the axes are $[100] \neq [110] = [1\bar{1}0]$; whereas for the 3T polymorph the axes are $[2\bar{1}\bar{1}0] = [\bar{1}2\bar{1}0] = [\bar{1}\bar{1}20]$. Plate VIII, A and B are zero-layer photographs about the $[100]$ and $[110]$ axes of a 1M phlogopite. The $[100]$ axis photograph shows the presence of a plane of symmetry. A 1M muscovite pattern differs only slightly in position and intensity of the reflections. Plate IX, C and D are zero-layer photographs about the $[2\bar{1}\bar{1}0]$ axis of a 3T phlogopite and muscovite. These have closely similar positions of the reflections but the intensities differ considerably. It will be seen that the 1M and 3T photographs are quite different and may be readily distinguished.

But a $5.3 \text{ \AA}$. axis rotation photograph of a 1M phlogopite twinned on $[110]$ or $[1\bar{1}0]$ will contain reflections on or very close to the positions occupied by the 3T reflections. If β is exactly equal to the ideal value, there will be no displacement from positions consistent with 3T symmetry. If β deviates from the ideal value, the reflections will lie on zigzags. If no displacement from trigonal geometry is visible, the twinning can still be detected if the three components connected by the twinning do not have equal volumes, for the intensities of the reflections will not agree with those for a 3T polymorph. If the volumes are equal the intensities will be equal to those for a 3T crystal. On the other hand a twinned 1M muscovite cannot give a photograph identical with a 3T muscovite, for the positions of the reflections will be considerably different since β does not have the value necessary for pseudo-trigonal geometry as described above.

The zero-layer b ($9.2 \text{ \AA.}$) axis Weissenberg (or precession) photographs of 1M and 3T phlogopite crystals are identical and cannot be used for identification purposes, because the reflections arising from the 3-layer repeat depend on distortion of the sub-cell and in the ideal trioctahedral structure have zero intensity. First- and second-layer b -axis photographs are suitable for identification purposes.

For routine identification of the mica polymorphs it is recommended that a powder photograph be taken first. This powder specimen may be obtained by grinding selected crystals or, if a focusing diffractometer is available, a slab of a fine-grained rock, cut perpendicular to the schistosity, serves as a suitable X-ray mount. The 1M and 3T structures of trioctahedral crystals will give identical powder patterns but can be resolved by single-crystal study. Complex polymorphs will be mistaken for simpler polymorphs since they give similar X-ray powder patterns, and the weak reflections that serve to identify them in single-crystal patterns will be lost in the background of a powder pattern. As the complex polymorphs appear to be rare and independent of specific pressure and temperature conditions, it may not be critical to obtain a positive identification in routine work. If identification or knowledge of twinning is desired, single-crystal photographs must be taken.

Acknowledgements.—The writers are indebted to the many investigators who donated specimens to this study. Discussions with Dr. S. B. Hendricks and Professor W. Dekeyser were of considerable help in the formulation of the theory. In addition, criticism of the manuscript by Drs. G. Donnay, H. P. Eugster, and S. B. Hendricks is gratefully acknowledged.

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A

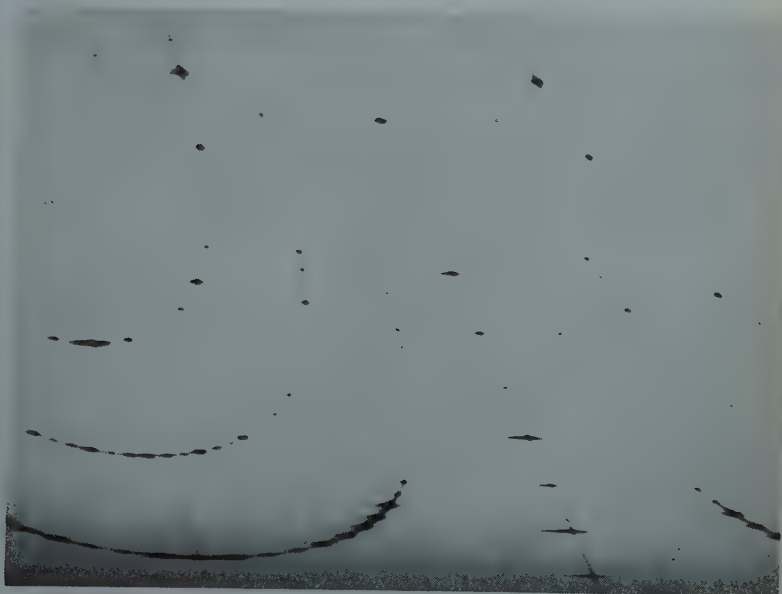


B





C



D

J. V. SMITH AND H. S. YODER: MICA POLYMORPHS



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EXPLANATION OF PLATES VIII AND IX.

Zero-layer Weissenberg photographs of micas about rotation axes with 5.3 Å. repeat distance. Filtered Co-K α radiation. The straight rows contain the basal reflections.

PLATE VIII.

FIG. A. 1M phlogopite, [100] axis; specimen 149.

FIG. B. 1M phlogopite, [110] axis; specimen 149.

The most striking difference between figs. A and B is the plane of symmetry in A. In these two figures the diffuse reflections between the (00 l) reflections are probably caused by parallel growth of another layer mineral. In the first curved row there are also some weak reflections from another layer mineral, or reflections from a small amount of a complex mica polymorph in parallel orientation with the 1M crystal, but they are somewhat irregular in position and no certain identification was possible.

PLATE IX.

FIG. C. 3T phlogopite, [2 $\bar{1}$ 10] axis; specimen R4463.

FIG. D. 3T muscovite, [2 $\bar{1}$ 10] axis; specimen Sultan Basin.

In figs. C and D note the uniform rise and fall of intensities in the rows of the 3T phlogopite, C, in contrast to the irregular sequence for the 3T muscovite, D.

Manganese silicate minerals from Chikla, Bhandara District, India.

By S. A. BILGRAMI, B.Sc., Ph.D., A.I.S.M., F.G.S.

Department of Geology, University of Manchester.

[Read 22 March 1956.]

Summary.—Blanfordite (a manganiferous aegirine), rhodonite, alurgite, manganophyllite, and piemontite are described from a pegmatite that cuts a manganese ore band in the Sitasaongi mine, Chikla, Bhandara district, India. In addition, rhodonite and piemontite are described from gneiss and schist areas. Chemical analyses and optical properties of all these minerals are given and their possible origin suggested.

THE minerals described in this paper were collected during the summer of 1950 from Sitasaongi mine, Chikla area, Bhandara district, India, which produces high-grade manganese ore. The ore band is 8 to 18 feet thick and is strongly folded and faulted. The associated rock types are calc-granulites, calc-gneisses, mica-schists, quartzites, gondite (quartz-spessartine rock), injection gneisses, and pegmatites. The pegmatites are the youngest and cut through the ore band as well as the country rocks. All are of Archaean age.

Previous work. The first detailed reference to the occurrence of manganese silicate minerals in India was made by Fermor (1909). He carried out preliminary optical work on these minerals and in a few cases chemical analyses were also undertaken. Blanfordite was first named and described by him on the basis of physical and optical properties and was analysed by Banerji (Hayden, 1916); Krishnan (1937) also reported the occurrence of the mineral in Gangpur State, India, but no detailed optical work was undertaken. A preliminary description of the mineral was given by the present writer in 1953.

The only work on the Indian piemontites is that of Fermor (1909), who has described the mineral from nine different localities from varying rock types. He gave comparisons of pleochroic schemes of the mineral from different localities but no other optical work was undertaken. A chemical analysis of the mineral from Kachi Dhana manganese mine, India, was given by Pascoe (1930).

Occurrence. At the 60-foot level of the Sitasaongi mine the ore band

and the mica-schist (which forms the foot-wall and the hanging-wall sides of the ore band) are cut by a pegmatite about 4 feet thick. The minerals described here occur irregularly distributed in the pegmatite, with a large number of braunite xenoliths. Here the minerals are associated with manganese amphiboles (Bilgrami, 1955), quartz, oligoclase, microcline, braunite, and a little baryte. Blanfordite occurs as brown crystals measuring up to $\frac{1}{2}$ inch in length; most of the crystals show well-developed faces and can be easily distinguished by their habit from other minerals of the pegmatite. Rhodonite occurs in small lumps of pink colour and sugary texture. Alurgite and manganophyllite attain large dimensions and books measuring up to 3 inches across can be found. Piemontite is developed in chocolate-brown crystal masses, some of them measuring up to 3 inches by 2.5 inches by 1.6 inches. Rhodonite and piemontite also occur in the schist and the gneiss areas, where rhodonite forms veins and patches in rhodonite-quartz-spessartine rock, while the piemontite-bearing bands, which are 1 to 2 inches thick, are composed of piemontite, quartz, manganese ore, sphene, biotite, and apatite.

Description and chemistry of the minerals.

Blanfordite is a monoclinic pyroxene the colour of which varies from lavender-blue to brown in the hand-specimen; the specific gravity is 3.28 and the hardness is $6\frac{1}{2}$ –7. In thin section the mineral is deep pink in colour but occasionally shows a bleached appearance in different parts of the same plate. It is pleochroic from pink to blue according to the scheme given in table I, and has a high birefringence and patchy polarization colours. Schiller inclusions of brown colour arranged parallel to the prismatic cleavages are present and alteration to a dense brown material, probably limonite, is common (fig. 1). The mineral does not show variation from the type specimen from Kacherwahi, India.

The chemical analyses of the mineral from Sitasaongi and Kachi Dhana manganese mines are given in table I. The two analyses are very similar and the formula calculated on the basis of 6 oxygen atoms can be expressed as $(\text{Na,Ca})_{0.89}(\text{Al,Ti,Fe,Mn})_{1.08}(\text{Si,Al})_{2.00}\text{O}_6$, which corresponds closely to the ideal formula XYSi_2O_6 , and is near the boundary suggested for aegirine by Sabine (1950); blanfordite could therefore be classed as a manganiferous aegirine.

Rhodonite from the pegmatite is rose-pink in colour, has sugary texture and vitreous lustre; the specific gravity is 3.66 and the hardness is $6\frac{1}{2}$. In thin section the mineral shows granular texture, consisting of

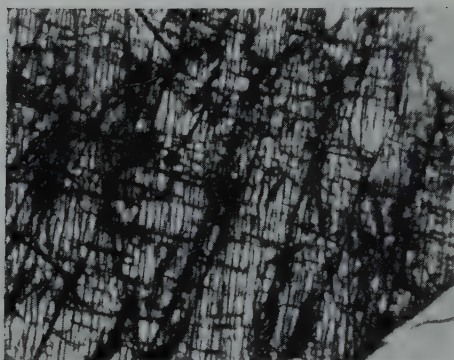
FIG. 1. Blanfordite showing veins of alteration product. $\times 70$.

TABLE I. Chemical analyses and optical properties of blanfordites and rhodonites.

1-4, percentage compositions, 1a-4a, same analyses calculated to a basis of 6 oxygen atoms. Al^{iv} and Al^{vi} , Al in fourfold and sixfold coordination respectively.

	1.	2.	3.	4.		1a.	2a.	3a.	4a.
SiO_2 ...	52.52	52.18	45.46	48.38	Si ...	1.96	1.95	1.98	2.01
Al_2O_3 ...	5.88	5.89	0.27	0.09	Al^{iv} ...	0.04	0.05	0.01	0.00
TiO_3 ...	0.59	—	nil	0.02	Al^{vi} ...	0.20	0.21	nil	0.00
Fe_2O_3 ...	18.15	20.26	nil	0.21	Ti ...	0.01	nil	nil	0.00
FeO ...	1.11	—	0.96	11.31	Fe^{iii} ...	0.51	0.57	nil	0.00
MgO ...	3.26	3.25	0.55	1.87	Fe^{ii} ...	0.03	nil	0.04	0.39
MnO ...	4.72	3.60	50.54	31.54	Mg ...	0.19	0.18	0.00	0.11
CaO ...	4.38	4.37	2.25	6.62	Mn ...	0.14	0.11	1.86	1.19
K_2O ...	nil	nil	nil	0.02	Ca ...	0.18	0.17	0.10	0.30
Na_2O ...	9.75	10.12	nil	nil	K ...	nil	nil	nil	0.00
$\text{H}_2\text{O} + \dots$	nil	—	nil	0.07	Na ...	0.71	0.75	nil	0.00
$\text{H}_2\text{O} - \dots$	nil	—	nil	0.02	OH ...	nil	nil	nil	0.02
	100.36	99.67	100.03	100.15	$X + Y^*$	1.97	1.99	2.00	1.99
α ...	1.732	—	1.725	1.722					
β ...	1.756	—	1.728	1.725					
γ ...	1.770	—	1.736	1.734					
$\gamma - \alpha$...	0.038	—	0.011	0.012					
$\gamma : c$...	9°	—	36°	35°					
2V ...	80°	—	74°	71°					
Sp. gr.	3.28	—	3.66	3.64					

* Sum of cations other than Si and Al^{iv} .

1. Blanfordite, Chikla, India. Analyst, R. K. Phillips. Pleochroism, α rose-pink, β pale blue, γ blue.

2. Blanfordite, Kachi Dhana, India. Analyst, A. K. Banerji (Hayden, 1916). Pleochroism, α rose-pink, β bluish-lilac, γ sky-blue.

3. Rhodonite from pegmatite, Chikla, India. Analyst, R. K. Phillips. Pleochroism, α pale pink, β pale pink, γ pink.

4. Rhodonite from gneiss, Chikla, India. Analyst, S. A. Bilgrami. Colourless.

pale pink to colourless, rounded crystals. Most of the sections show one set of prismatic cleavages but occasionally two sets almost at right angles are observed. In grains and thick sections the mineral is pleochroic from pale pink to colourless. It is often altered along cracks and cleavages to a dirty brown material, possibly psilomelane.

Rhodonite from the gneiss does not show much difference from the above in thin section but polysynthetic twinning on (010) is occasionally observed; the twin lamellae are of equal thickness and are regularly spaced. Alteration to a dense brown mass is more marked here than in the pegmatite specimen, and may go so far that the hand-specimen is dark brown. The alteration usually seems to start along the cleavages and then spreads in all directions leaving small areas of clear unaltered mineral surrounded by dense brown manganese ore, possibly psilomelane; in some cases the alteration does not seem to start from the cleavages but spreads all over the mineral in moss-like form clouding the whole crystal. The alteration product is not of uniform colour but is often dark and light brown in patches. The associated minerals in the gneiss are lemon-yellow spessartine and quartz. The garnet is clear and seems to alter less readily than the rhodonite. In the much altered specimens the garnet also shows areas of dark brown alteration product and it appears that the alteration products of the two minerals are alike.

The chemical analyses and optical properties of rhodonites are given in table I. The atomic ratios have been calculated on the basis of 6 oxygen atoms to illustrate the relationship with the pyroxene group. It will be seen that the pegmatite mineral shows lower Si, Fe", and Ca content but much higher Mn; in fact rhodonites with such high Mn content are very rare. These differences in the chemistry of the two specimens are reflected in their optics, the rhodonite with higher Mn + Fe" content having higher refractive indices.

Alurgite occurs as books up to 3 inches broad in the pegmatite. It is dark reddish-brown in colour and splits easily into thin smoky brown flakes along the cleavages. Under the microscope thin plates of the mineral are pale brown with a pinkish tint and pleochroic from pale brownish-yellow to reddish-brown.

The chemical analyses and optical properties of the Chikla alurgite are given in table II. The two analyses of the mineral from Sitasongi mine show general similarity but some important differences in detail, thus the earlier analysis shows higher SiO_2 , Al_2O_3 , and lower MgO ; TiO_2 and Na_2O are not recorded in the earlier analysis but are present in

substantial amounts in the present analysis. Penfield's analysis of the mineral from the type locality shows very high SiO_2 compared with the two Sitasaongi specimens. The atomic ratios calculated on the basis of $12(\text{O},\text{OH})$ are included in table II and give the composition: $(\text{K},\text{Na},\text{Ca})_{1.09}(\text{Al},\text{Ti},\text{Fe},\text{Mg},\text{Mn})_{2.30}(\text{Si},\text{Al})_{4.00}\text{O}_{10.06}(\text{OH})_{1.94}$. The alurgite

TABLE II. Chemical analyses and optical properties of alurgites and manganophyllites.

1-5, percentage compositions; 1a and 4a recalculated to a basis of $12(\text{O},\text{OH})$. Al^{iv} and Al^{vi} , Al in fourfold and sixfold coordination respectively. $X = \text{Na} + \text{K} + \text{Ca}$, $Y = \text{Al}^{\text{vi}} + \text{Ti} + \text{Fe}^{\text{iii}} + \text{Mg} + \text{Fe}^{\text{ii}} + \text{Mn}$.

	1.	2.	3.	4.	5.		1a.	4a.
SiO_2 ...	40.60	45.6	53.22	38.32	40.6	Si ...	2.84	2.79
Al_2O_3 ...	26.37	29.6	21.19	16.51	16.7	Al^{iv} ...	1.16	1.21
TiO_2 ...	1.40	—	—	1.54	1.0	Al^{vi} ...	1.02	0.20
Fe_2O_3 ...	6.38	5.8	1.22	5.76	5.1	Ti ...	0.07	0.08
FeO ...	0.22	—	—	1.20	—	Fe^{iii} ...	0.34	0.31
MgO ...	7.42	2.23	6.02	14.82	20.33	Fe^{ii} ...	0.01	0.07
Mn_2O_3 ...	nil	1.07	0.87	nil	—	Mg ...	0.77	1.60
MnO ...	1.53		0.18	6.24	5.58	Mn ...	0.09	0.39
CaO ...	0.21	0.98	—	0.95	0.78	Ca ...	0.02	0.07
K_2O ...	9.46	9.5	11.20	9.23	8.40	K ...	0.84	0.86
Na_2O ...	1.66	—	0.34	1.37	—	Na ...	0.23	0.19
$\text{H}_2\text{O} +$...	4.15	4.4	5.75	4.22	2.2	OH ...	1.94	2.04
$\text{H}_2\text{O} -$...	0.31	—	—	0.25	—			
	<u>99.71</u>	<u>99.18</u>	<u>99.99</u>	<u>100.41</u>	<u>100.69</u>	Y ...	2.30	2.65
						X ...	1.09	1.12

1. Alurgite, Chikla, India. Analyst, S. A. Bilgrami. α 1.588, β 1.636, γ 1.636, $\gamma - \alpha$ 0.048, $2V$ 3° , Sp. gr. 2.98.

2. Alurgite, Chikla, India. Analysts, Sahu and Dave (Kilpady and Dave, 1954). β 1.62-1.63, $\gamma - \alpha$ 0.038-0.04, $2V$ $29^\circ 15'$.

3. Alurgite, Piemont, Italy. Analyst, S. L. Penfield (Penfield, 1893).

4. Manganophyllite, Chikla, India. Analyst, S. A. Bilgrami. α 1.575, β 1.617, γ 1.621, $\gamma - \alpha$ 0.046, $2V$ 30° , Sp. gr. 2.98.

5. Manganophyllite, Chikla, India. Analysts, Sahu and Dave (Kilpady and Dave, 1954). β 1.60-1.61, $\gamma - \beta$ 0.0056, $2V$ $35^\circ 30'$.

analyses show more cations than are appropriate for a dioctahedral mica (2.30 instead of 2). Winchell (1951) has classified alurgite as a manganiferous phengite but pending a new study of the mineral from the type locality it would be better not to attempt to classify it.

Manganophyllite has the same mode of occurrence as alurgite with which it can easily be confused. In thin section it is pleochroic from pale yellowish-brown to dark brown and is occasionally partially replaced by a colourless tremolite.

The two manganophyllites from the Sitasaongi mine show close similarity in their chemical composition (table II) except for much higher MgO and lower MnO, K₂O, and H₂O, and the absence of Na₂O in the earlier analysis. The atomic ratios of the mineral calculated on the basis of 12(O,OH) give the formula:



which is in general agreement with the structural formula for the ferro-magnesian micas. The high magnesia content of the mineral suggests a close relationship with phlogopite. The manganophyllite described by Jakob (1925) is classified by Winchell (1951) as a ferric iron equivalent of phlogopite, but both would be more precisely named mangani-ferous biotite.

Piemontite. The piemontite from the schist is granular in form, ruby red, and has pearly lustre. In thin section the mineral is pink or lemon-yellow in colour, idioblastic in form and encloses grains of braunite, quartz, and sphene. Areal analyses of the schist show that the mineral forms between 43 and 45 % of the rock, the other minerals present being quartz, manganese ore, sphene, biotite, and apatite. The pegmatite specimen is dark brown in colour, striated in the zone [001], and has a metallic lustre. In thin section piemontite is seen to occur as large plates often peppered with manganese ore grains and showing perfect basal cleavages. It is deeply coloured and strongly pleochroic according to the scheme given in table III. Occasional inclusions of a pink-coloured idiomorphic mineral with lower refractive index may be thulite.

The chemical analyses of the two piemontites with comparisons are given in table III. The three piemontites from India show exceptionally high Mn content, while the piemontite from St. Marcel shows very high Mn^{III} content but is well below the piemontite from the Sitasaongi pegmatite. The formulae of the Chikla piemontites calculated on the basis of 13(O,OH) are given in table III; it will be seen that the two specimens show close similarity except that the pegmatite specimen has higher Mn^{III}, Al, and Ca, and lower Mg. The piemontite from the schist shows some noteworthy features, particularly its high alkali content and the presence of Cu in small amounts; a search of the literature has failed to disclose a piemontite with comparable alkali content. In order to conform to the usually accepted structural formula for the epidote group it is necessary to distribute Mn^{III} between the X and the Y positions.

TABLE III. Chemical analyses and optical properties of piemontites.

1-4, percentage compositions; 1a and 2a, analyses 1 and 2 recalculated to a basis of 13(O,OH). X = (sum of all cations) - (cations in sixfold coordination). Al^{iv} and Al^{vi} , Al in fourfold and sixfold coordination respectively.

	1.	2.	3.	4.		1a.	2a.	
SiO ₂ ...	36.60	36.63	35.57	38.64	Si ...	2.92	2.89	} 3.00
Al ₂ O ₃ ...	15.24	17.21	18.27	15.03	Al ^{iv} ...	0.08	0.11	
TiO ₂ ...	0.60	0.21	—	—	Al ^{vi} ...	1.37	1.49	} 3.00
Fe ₂ O ₃ ...	7.04	6.85	7.06	8.38	Ti ...	0.03	0.01	
Mn ₂ O ₃ ...	14.93	17.78	12.43	15.00	Fe ⁱⁱⁱ ...	0.42	0.41	
MnO ...	nil	nil	2.94	—	Mg ...	0.35	0.10	
MgO ...	2.92	0.85	0.96	—	Cu ...	0.01	nil	
CaO ...	17.47	18.98	19.53	22.19	Mn ⁱⁱⁱ ...	0.82	0.99	}
Na ₂ O ...	2.41	nil	1.14	—		0.31	0.35	
K ₂ O ...	0.95	nil	0.87	—	Ca ...	1.48	1.60	
H ₂ O + ...	1.95	1.75	0.85	1.78	Na ...	0.37	nil	
H ₂ O - ...	—	—	0.38	—	K ...	0.09	nil	
CuO ...	0.31	—	—	—	OH ...	1.01	0.91	
	100.42	100.26	100.00	101.02	X ...	2.26	1.95	

1. Piemontite from schist, Chikla, India. Analyst, R. K. Phillips. Analysis on powder dried at 105° C. α 1.785, β 1.796, γ 1.808, $\gamma - \alpha$ 0.023, $\gamma : c$ -7°, 2V 74°. Twinned on {100}. Pleochroism, α yellow, β pale pink, γ deep pink.

2. Piemontite from pegmatite, Chikla, India. Analyst, R. K. Phillips. Analysis on powder dried at 105° C. α 1.794, β 1.807, γ 1.819, $\gamma - \alpha$ 0.025, $\gamma : c$ -9°, 2V 79°. Pleochroism, α brownish-yellow, β violet-pink, γ ruby-red, violet.

3. Piemontite from Kajlidongri, India. Analyst not stated. Pascoe, 1930.

4. Piemontite from St. Marcel. Analyst, Rammelsberg, 1875.

Relation between chemical composition and optical properties.

A brief review of the literature on the subject has been made in a previous paper (Bilgrami, 1955) and only a short reference to some important points will be made here. Sabine (1950) has discussed in detail the relationship of the chemical composition and the optical properties in the acmitic pyroxenes. He states that, 'The range of composition shown by minerals having similar optical properties appears to arise principally from replacement of Mgⁱⁱ and Feⁱⁱ by each other.' Specific gravity, extinction angle, and refractive index (β) vary irregularly within limited ranges. In the case of blanfordite, as in aegirine, the high Feⁱⁱⁱ and Na content will have considerable influence on the optical properties of these minerals. Sundius (1931) has published graphs showing relations between refractive indices, optic axial angle, and (Ca,Mg)SiO₃ and (Mn,Fe)SiO₃ in rhodonites. He has shown that with an increase in (Mn,Fe)SiO₃ indices of refraction and optic axial angles increase. Also in his opinion MgSiO₃ reduces refractive indices, optic axial angle, and specific gravities. On the other hand, FeSiO₃ is said to counteract the

effect of MgSiO_3 . It may be pointed out that in most rhodonites the amount of MgSiO_3 is too small to have any significant influence on the optical properties and it is likely that the combined influence of MgSiO_3 and CaSiO_3 is more significant. In the two rhodonites under discussion here it is seen that a substantial decrease in the Mn content of the rhodonite from gneiss is accompanied by a decrease in the γ value even though this specimen has a higher Fe'' content than the pegmatite specimen.

The relationship between the chemical composition and optical properties of epidotes is not well known. Short (1933) has published a diagram plotting the optical properties against the Mn''' contents of the piemontites. His diagram shows that the specific gravity, the optic axial angle and $\gamma:c$ all increase with an increasing content of Mn''' , while the refractive indices decrease. The highest γ value given by Short is for a piemontite with 10 % Mn''' . It is clear that the relationship of the optical properties and chemical composition has been oversimplified by Short, as other ions such as Al, Fe, and Ca which are present in substantial amounts will also affect the optical properties of the mineral. Johnston (1949) has shown that in clinozoisites the refractive indices and specific gravity increase with an increasing content of Fe_2O_3 but the optic axial angle and $\alpha:c$ vary irregularly when the Fe_2O_3 content of the mineral is below 5 %. He has suggested that when the iron content is low such factors as the pressure and temperature prevailing during the period of crystallization exert greater influence on the optical properties than does the chemical composition of the mineral. The two new analyses show that the specific gravity, refractive indices, $2V$, and $\gamma:c$ all increase with an increasing content of Mn''' in the piemontites.

Paragenesis.

In discussing the origin of rhodonite, Fermor (1909) advocated an igneous origin for this mineral. The absence of rhodonite from the typical kodurite rocks and those intrusive into gondites has been explained by him as due to the fact that 'rhodonite requires about 42 % of manganese for the formation of pure MnSiO_3 and when many other constituents are present in the rock so that the percentage of manganese is relatively low, the manganese naturally forms silicates that contain small percentages of manganese such as the other mangani-ferous pyroxenes and manganese garnets'. In the present case, however, rhodonite is found in the rocks intrusive into the gondite series. It appears that the formation of this mineral is due to the assimilation of

manganese ore by the pegmatite that cuts through the ore band. Participation of other elements such as Al, Fe, Mg, and Ca would produce more complex manganese silicate minerals. As manganese was abundant a higher percentage of manganese in the minerals than is usual may be expected, this element replacing Ca, Fe, or Mg.

Acknowledgements.—Thanks are due to the Central Provinces Manganese Ore Co. Ltd., Nagpur, India, for having provided the author with all possible facilities during the field work, and to the Director, Geological Survey of India, for having kindly supplied the type specimen of blanfordite. This work has been carried out at the Geological Laboratories, University of Manchester, and the author is indebted to Professor W. A. Deer for constant encouragement, advice, and valuable criticism of the paper. Thanks are also due to Mr. R. K. Phillips for some of the new analyses.

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The Eskdalemuir tholeiite and its contribution to an understanding of tholeiite genesis.

By R. B. ELLIOTT, B.Sc., Ph.D., F.G.S.

Department of Geology, The University, Nottingham.

[Read 26 January 1956.]

Summary.—The Eskdalemuir tholeiite has the following modal composition: glass 42.2 %, felspar 24.4 %, pyroxene 30.6 %, magnetite 2 %, chlorite 1 %. The glass has been separated and analysed. It has 70 % SiO_2 and is of granitic composition. On a selected triangular diagram the plots of the Eskdalemuir rock, its residual glass, and its crystalline portion are spread along a narrow belt marking the compositions of the Tertiary tholeiites. Because the differences in the chemical compositions of the phases of the Eskdalemuir tholeiite are produced by crystallization, it is concluded that the variety of composition of the other Tertiary tholeiites is consistent with a genesis controlled by crystallization differentiation.

STRETCHING almost completely across the Lower Palaeozoic rocks of the Southern Uplands of Scotland is the north-west trending Eskdalemuir dyke, one of the great solitary Tertiary dykes of the south of Scotland. It appears on the southern edge of the Permian basin of the Snar valley, runs by Moffat to the vicinity of Langholm, a distance of almost 40 miles, and attains a width of 180 feet (Pringle, 1935).

In the past it has attracted the attention of many eminent petrologists who between them have investigated most of its aspects. Geikie (1880, 1897) described it fully and pointed out the salient petrographic character of a framework of basaltic minerals with interstitial glass (fig. 1); Teall (1888) figured it in 'British Petrography'; Tyrrell (1917) related it to other Tertiary dykes of the Clyde area; and Holmes and Harwood (1929) discussed its relationships to the tholeiites of the north of England. The only part which escaped direct investigation was the clear glassy base, which is present in sufficient quantity to be separated from its associated minerals and analysed.

The main purpose of this paper is to present the new analyses of tholeiite and mesostasis, to calculate the composition of the crystalline fraction, and to comment on the bearing of these analyses upon the genesis of the various members of the north of England and Scottish Tholeiite Series. Some new data on mineral composition and proportions are also given, but in view of the comprehensive literature it is not

proposed to repeat the rock descriptions but rather to add supplementary notes, which can be read in conjunction with the earlier work.



FIG. 1. Tholeiite composed of plagioclase, pyroxene, magnetite, and glass. The large crystal in the centre of the field is hypersthene rimmed by a clinopyroxene.

Petrology of the tholeiite.

The specimens used in this investigation were collected on Eskdalemuir at the summit of Castle Hill about 10 miles north-west of Langholm. They agree in every way with the hemicrystalline rock of the earlier descriptions and differ from samples of the dyke from other localities only in their superior freshness. They may therefore be taken as representative of the dyke as a whole.

The principal minerals are pyroxene, plagioclase, and glass, which, from point-counter analyses under high magnification at about ten thousand points, are present in the following proportions: glass

42.2 ± 0.6 , feldspar 24.4 ± 0.5 , pyroxene 30.6 ± 1.0 , magnetite 2 %, chlorite 1 %.

Feldspars. The phenocrysts and smaller crystals alike are almost exclusively labradorite. Each crystal is slightly zoned and has a bulk composition of $\text{Ab}_{46}\text{An}_{54}$. So far as I could determine anorthite is completely absent and only one bytownite crystal, $\text{Ab}_{25}\text{An}_{75}$, was seen in all the thin sections examined. This was within a small cluster of labradorites.

Pyroxenes. The phenocrysts are of hypersthene, rimmed with monoclinic pyroxene, and pigeonite in approximately equal amounts and the small granules are of pigeonite and augite. Dr. I. D. Muir who has taken an interest in the pyroxenes has supplied the following details:

There are four distinct pyroxene phases (all compositions as atomic percentages) (fig. 2).

H—Hypersthene occurs as practically unzoned microphenocrysts, stout subhedral grains mostly jacketed by a discontinuous mantle of grains of monoclinic pyroxene. Where the identity of this mantling pyroxene has been established it has always proved to be pigeonite ($\beta \perp (010)$; average $2V = 15^\circ$ but strongly zoned). The hypersthene has $2V_\alpha = 68^\circ$ – 66° and the probable composition is $(\text{Ca}_{0.05}\text{Mg}_{0.69}\text{Fe}_{0.26})\text{SiO}_3$.

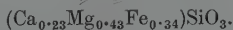
P—Pigeonite occurs as practically unzoned microphenocrysts, stout subhedral greenish grains which are never jacketed. These have $\alpha = 1.687$, $\beta = 1.688$, $\gamma = 1.714$; $2V_\gamma = 19^\circ \rightarrow 14^\circ$ margin; $\alpha \perp (010)$; $\gamma \wedge c = 43^\circ$. The probable composition is $(\text{Ca}_{0.09}\text{Mg}_{0.60}\text{Fe}_{0.31})\text{SiO}_3$.

Q—Pigeonite is present in the groundmass as little greenish columnar prisms with cross fractures and strong zoning. These comprise about one quarter of the finer-grained pyroxene. They have $\beta = 1.696$ – 1.702 (approximate values), $\gamma = 1.731$ (maximum value), $2V_\gamma = 10^\circ \rightarrow 28^\circ$ margin (average value 20°); $\beta \perp (010)$. The range of composition is from $(\text{Ca}_{0.19}\text{Mg}_{0.46}\text{Fe}_{0.35})\text{SiO}_3$ to $(\text{Ca}_{0.24}\text{Mg}_{0.39}\text{Fe}_{0.37})\text{SiO}_3$.

R—Subcalcic augite is present as discrete roundish brownish grains which are practically unzoned. They have $\beta = 1.702$ (approximate value); $2V_\gamma = 45^\circ \rightarrow 38^\circ$ (margin), average value 42° ; $\beta \perp (010)$; $\gamma \wedge c = 41^\circ$. The composition is



The normative pyroxene is



Glass. This is mainly pale brown and completely transparent with very few inclusions or microlites. A small proportion of it is slightly clouded and a very few small patches are bright orange in colour, due, according to Vincent (1950), to incipient alteration. The specific gravity of the clear brown part is 2.38 and the refractive index is 1.500 ± 0.004 .

Magnetite occurs as small scattered euhedra.

The chemical composition of the tholeiite is given in table I and it is clear that it is andesitic in spite of the basaltic nature of the crystals.

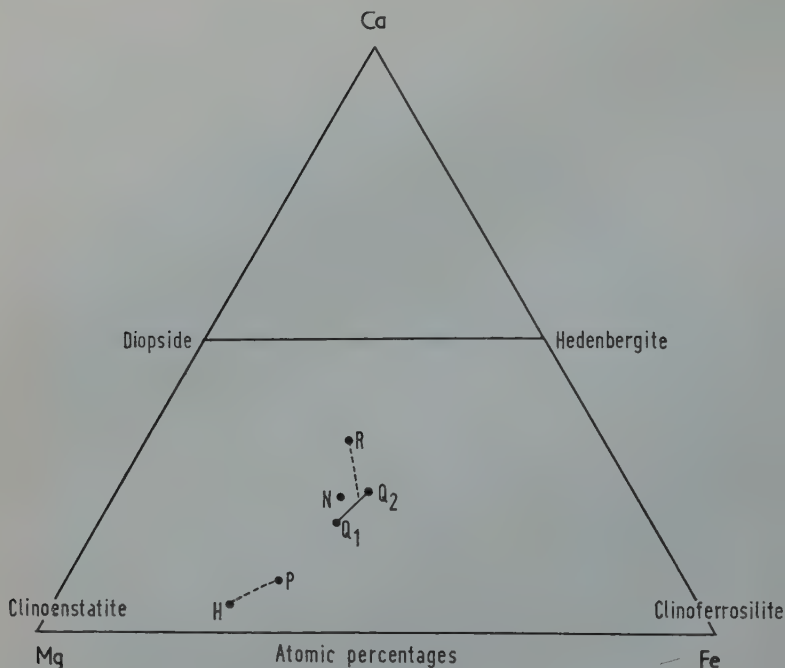


FIG. 2. Plot of the modal pyroxenes of the Eskdalemuir tholeiite. *H*, hypersthene microphenocrysts; *P*, pigeonite microphenocrysts; *Q*₁ and *Q*₂, limiting compositions of the groundmass pigeonite; *R*, subcalcic augite of the groundmass; and *N*, normative pyroxene of the crystalline material. Tie lines, - - -, indicate the phases in equilibrium.

For a comparison with other Tertiary tholeiites the reader is referred to Holmes and Harwood (1929).

Tyrrell (1917) has discussed the nomenclature of rocks of this sort and has suggested the possibility of the name 'cumbraite of Eskdalemuir type'. Holmes on the other hand regards it pretty definitely as a minor variant of the Cleveland type of tholeiite but admits that if it should ever be thought necessary to split it off from the Cleveland group then Tyrrell's term of 'Eskdalemuir type' could be used.

The residual glass.

The glass concentrate was prepared as follows. The rock was first crushed to pass a 300-mesh sieve, after which the rock flour of fine silt and clay grade was washed away with water by decantation.

Separation was done in two stages; initially in a beaker with a bromoform-acetone mixture of sp. gr. 2.6 and secondly in a centrifuge with a mixture of sp. gr. 2.42. It was necessary to centrifuge many times to reach a purity of 98 %. At this stage, considered sufficiently clean for analysis, the impurities were in part felspar, in part pyroxene, and in part an indeterminate reddish-brown substance.

TABLE I. Chemical compositions of the Eskdalemuir dyke and of its components.

Chemical compositions.				Norms.			
	A.	B.	C.		A.	B.	C.
SiO ₂ ...	60.22	70.58	53.4	Q	14.46	35.04	1.62
Al ₂ O ₃ ...	14.06	11.62	15.3	or	8.34	18.30	3.06
FeO ...	6.58	1.52	9.5	ab	24.60	28.80	22.53
Fe ₂ O ₃ ...	0.90	1.35	0.63	an	21.10	5.84	28.08
TiO ₂ ...	0.64	0.65	0.63	C	nil	0.51	nil
MnO ...	0.08	0.02	0.10	wo	6.38	nil	10.56
CaO ...	7.36	1.36	10.75		3.20	nil	5.20
MgO ...	4.28	0.72	6.3	di {	3.17	nil	5.15
K ₂ O ...	1.36	3.10	0.34	en ...	7.50	1.80	10.60
Na ₂ O ...	2.95	3.44	2.64	hy {	7.12	0.53	10.82
H ₂ O— ...	0.22	nil	0.34	fs ...	1.39	2.09	0.93
H ₂ O+ ...	1.53	4.98	nil	mt ...	1.21	1.22	1.22
CO ₂ ...	nil	nil	nil	il ...	0.34	0.34	nil
P ₂ O ₅ ...	0.11	0.18	0.06	ap ...	1.75	4.98	0.34
	100.29	99.52	99.99	H ₂ O ...	100.56	99.45	100.11

A, Eskdalemuir tholeiite (Anal. W. H. Herdsman).

B, glass from Eskdalemuir tholeiite (Anal. W. H. Herdsman).

C, calculated composition of crystalline phase of Eskdalemuir tholeiite (from columns A and B).

The chemical analysis and norm are given in table I along with those of the parent tholeiite. One affinity is clear, the glass is approximately 'granitic' in composition and this is emphasized by the fact that it falls within the field of analysed granites plotted in terms of their normative Or, Qz, and Ab (Carnegie Institute of Washington Year Book no. 51). More local affinities are appreciated by comparing the analyses with existing analyses of pitchstones, leidleites, inninmorites and of the various other members of the Tholeiite Series (Tyrrell, 1917). In general, comparisons are facilitated by the use of triangular diagrams chosen with care to emphasize important composition variations and to eliminate subsidiary fluctuations. In the case of the tholeiite series there is only insignificant Fe enrichment and the standard



diagram is consequently not satisfactory. On the other hand, the felspars

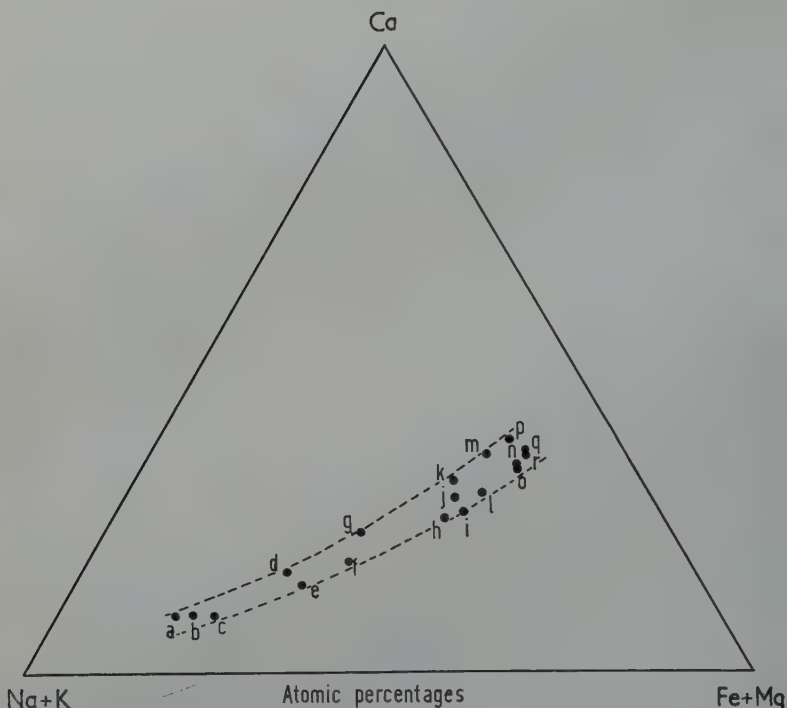


FIG. 3. Plot of the chemical compositions of Tertiary tholeiites.

- a*, pitchstone. Glen Shurig type. The Geology of Arran, p. 234.
- b*, pitchstone. Judd's No. II dyke. Ibid.
- c*, residual glass from Eskdalemuir dyke. New analysis.
- d*, inninmorite. Pitchstone II. The Geology of Ardnamurchan, N.W. Mull and Coll, p. 84.
- e*, inninmorite. Pitchstone I. Ibid.
- f*, inninmorite. Tyrrell, 1917, p. 310.
- g*, leidleite III. The Tertiary and Post-Tertiary Geology of Mull, &c., p. 19.
- h*, leidleite II. Ibid.
- i*, tholeiite of Cleveland type, Cleveland dyke. Holmes and Harwood, 1929, p. 39.
- j*, tholeiite of Cleveland type, Eskdalemuir dyke. New analysis.
- k*, tholeiite of Cleveland type, Hebburn dyke. Holmes and Harwood, 1929, p. 35.
- l*, tholeiite of Acklington type, Acklington dyke. Ibid., p. 31.
- m*, tholeiite of Acklington type, Coley Hill dyke. Ibid., p. 32.
- n*, tholeiite of Salen type, Kielderhead dyke. Ibid., p. 15.
- o*, calculated composition of crystals of the Eskdalemuir dyke.
- p*, tholeiite of Brunton type, Tynemouth dyke. Ibid., p. 21.
- q*, tholeiite of Talaidh type, Kielder Viaduct dyke. Ibid., p. 27.
- r*, tholeiite of Brunton type, Bingfield dyke. Ibid., p. 18.

clearly have a large role in tholeiite evolution and this factor must be taken into account. The diagram finally selected for use here was one using atomic percentages of Ca, Na + K, and Mg + Fe as triangular coordinates (fig. 3). This has two main advantages; firstly, the plotting of

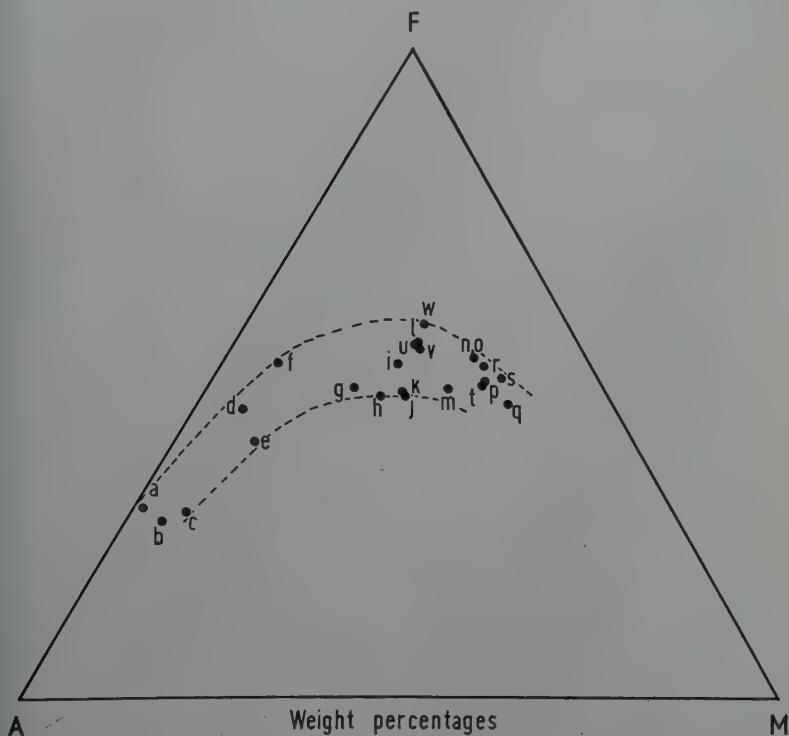


FIG. 4. Plot of the chemical compositions of tertiary tholeiites for the oxides $\text{FeO} + \text{Fe}_2\text{O}_3$ (F), MgO (M), alkalis (A). Data as for fig. 3 supplemented by:

- s, tholeiite of Talaidh type, Crookdene dyke. Holmes and Harwood, 1929, p. 28.
- t, tholeiite of Talaidh type, Collywell dyke. Ibid., p. 28.
- u, tholeiite of Cleveland type, Great Ayton. Ibid., p. 40.
- v, tholeiite of Cleveland type, Armathwaite. Ibid., p. 40.
- w, tholeiite of Cleveland type, Teesdale. Ibid., p. 40.

Ca allows the part played by the feldspars to be fully recorded, and secondly, the use of atomic percentages eliminates the constant oxygen which only diminishes the pictorial amplitude of the variations as shown on the triangular diagram. The standard AFM diagram is also given for comparison (fig. 4).

On the diagram selected the entire Tholeiite Series, including the

Eskdalemuir dyke, lie on a well-defined belt with surprisingly little scatter. The plots both of the residual glass and of the crystals of the Eskdalemuir tholeiite also fall on and at opposite ends of the same belt. From these observations it seems at least logical to conclude that the process that operated within the single tholeiite to produce the contrasted compositions of crystals and glass could have operated on a larger scale to produce the several members of the tholeiite series. The process that took place within the tholeiite was crystallization. It is therefore concluded that the Tholeiite Series was probably the product of fractional crystallization.

Before this hypothesis can be accepted as a reasonable possibility the objections to it, put forward by Holmes (1929), must first be answered. These objections are:

1. The chemical composition of the crystals in one of the low SiO_2 tholeiites (Bingfield dyke) does not agree with the theoretical composition required to be extracted from that tholeiite to form other tholeiites of higher SiO_2 content.

2. Pyroxene crystallization in each of the tholeiites begins with hypersthene, whereas in a series of successive residual magmas this would not be expected.

3. The anorthite content of the plagioclase does not fall with the rise in the felspar ratio.

4. The $F/(P+F)$ ratio¹ only reaches that of the Whin Sill (quartz-dolerite) whereas in a residual product it ought to be higher.

5. The $\text{MgO}/(\text{MgO}+\text{FeO})$ ratio is higher in some of the high SiO_2 tholeiites than it is in some of the lower SiO_2 tholeiites.

These objections can be answered severally in the following manner:

1. The evidence of the Bingfield dyke, based upon estimated compositions, is contradicted by that of the Eskdalemuir dyke, based on measured compositions. The accuracy of estimated chemical compositions of rocks depends upon the accuracy of two measurements, those of mineral composition and mineral frequency. In the Bingfield dyke it could be objected that neither of these measurements can be made with great precision; the felspars are zoned and somewhat variable and the relative quantities of the several pyroxenes present are unknown. In addition the micrometric analysis of such a fine-grained rock has inherent inaccuracies. Under these circumstances the estimated compositions of the phases cannot be considered to be known with certainty

¹ F = modal felspar, P = modal pyroxene.

and it is felt that conclusions drawn from them should be discounted when specifically contradicted by those of the measured Eskdalemuir rock.

2. Modern theory about the pyroxenes holds that hypersthene is stable under intratelluric conditions of crystallization so that the presence of this mineral throughout the Tholeiite Series can be explained by some crystallization prior to high-level intrusion. The groundmass pyroxenes, which crystallized under different conditions, are all monoclinic.

3. The chemical and petrographic evidence are at variance on this point. I cannot comment on the petrography of the whole series, but the conclusions to be drawn from the chemical data plotted on the triangular diagram are quite clear; they are that later members of the series have less Fe+Mg, i.e. less coloured minerals, but a higher Na/Ca ratio. The apparent contradiction may be due to the fact that much of the feldspar is occult in the glass. If it should be true that the An content of the crystalline feldspar systematically increases with the number of feldspar crystals we would have a phenomenon to tax any postulate of petrogenesis severely.

4. The low $F/(P+F)$ ratio is due to the presence of the glass which contains potentially a lot of feldspar. If the rock was fully crystallized then the ratio would be higher.

5. The $MgO/(MgO+FeO)$ ratio is variable, even haphazard, and there is no simple explanation of the variability. In terms of crystal fractionation it is possible to speculate on the role of magnetite. On any other genetic hypothesis the variability is equally or even more difficult to explain in simple terms. This criticism cannot, therefore, be levelled specifically at crystallization differentiation as the mechanism, but must apply equally to all the processes which have so far been postulated.

Conclusions.

The evidence from this study of the Eskdalemuir dyke goes a long way towards answering Holmes's objections to crystallization differentiation as the mechanism producing the range of compositions observed in the north of England tholeiites and by itself suggests that crystal fractionation has, in fact, been the important process.

There is nothing in the new data to disprove directly the hypotheses that the more basic tholeiites may be modified in the direction of a more granitic composition either by the incorporation of granitic material produced by the selective fusion of crustal rocks or by admixture with

a coexisting magma of granitic composition. On the other hand, should these hypotheses be accepted, the fact that the phases of the Eskdalemuir tholeiite fit the main tholeiite curve ceases to be significant and becomes merely an awkward coincidence.

In conclusion I would like to thank Dr. I. D. Muir for providing the detailed data on the pyroxene phases.

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The section $\text{CaSiO}_3\text{--MgSiO}_3\text{--Al}_2\text{O}_3$.

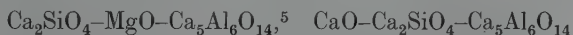
By E. R. SEGUNIT, M.Sc., Ph.D.

Department of Geology, University of Adelaide.¹

[Read 22 March 1956.]

Summary.—Phase relationships in the section $\text{CaSiO}_3\text{--MgSiO}_3\text{--Al}_2\text{O}_3$ through the quaternary system $\text{CaO--MgO--Al}_2\text{O}_3\text{--SiO}_2$ have been determined. The bearing of the results on the genesis of aluminous pyroxenes and associated minerals in metamorphic rocks is discussed.

AN investigation into the solid solution limits of alumina in the diopside-clinoenstatite series of pyroxenes² gave an opportunity to determine some of the phase relationships in the interior of the quaternary system $\text{CaO--MgO--Al}_2\text{O}_3\text{--SiO}_2$. A considerable amount of work has now been done on this system, so that a good picture of the equilibrium relationships is being built up. Results of work on the following parts of the system have been or are being published: anorthite-forsterite-silica,³ åkermanite-gehlenite,⁴



with 5 % MgO ,⁶ pseudowollastonite-åkermanite-gehlenite,⁷ pseudowollastonite-anorthite-diopside,⁸ gehlenite-spinel,⁹ diopside-forsterite-anorthite,¹⁰ sections with 5 %, 10 %, 15 %, 20 %, 25 %, 30 % Al_2O_3 ,¹¹ $\text{Ca}_2\text{SiO}_4\text{--Mg}_2\text{SiO}_4\text{--Ca}_5\text{Al}_6\text{O}_{14}$.¹²

¹ The greater part of this work was done whilst the author was a research student in the Dept. of Mineralogy and Petrology, University of Cambridge.

² E. R. Segnit, *Min. Mag.*, 1953, vol. 30, p. 218.

³ Olaf Andersen, *Amer. Journ. Sci.*, 1915, ser. 4, vol. 39, p. 407.

⁴ J. B. Ferguson and A. F. Buddington, *ibid.*, 1920, ser. 4, vol. 50, p. 131.

⁵ W. C. Hansen, *Journ. Amer. Chem. Soc.*, 1928, vol. 50, p. 2155.

⁶ H. F. McMurdie and Herbert Insley, *Journ. Res. Nat. Bur. Stand.*, 1936, vol. 16, p. 467.

⁷ E. F. Osborn and J. F. Schairer, *Amer. Journ. Sci.*, 1941, vol. 239, p. 715 [M.A. 8-258].

⁸ E. F. Osborn, *ibid.*, 1942, vol. 240, p. 751 [M.A. 9-16].

⁹ R. W. Nurse and N. Stutterheim, *Journ. Iron and Steel Inst.*, 1950, vol. 165, p. 137.

¹⁰ E. F. Osborn and D. B. Tait, *Amer. Journ. Sci.*, 1952, Bowen vol., p. 413 [M.A. 12-81].

¹¹ E. F. Osborn, R. C. DeVries, K. H. Gee, and H. M. Kraner, *Journ. Metals*, 1954, vol. 6, p. 33.

¹² E. R. Segnit and J. H. Weymouth, unpublished work.

The section pseudowollastonite-clinoenstatite-alumina, the subject of this paper, cuts through the centre of the four-component system from the Al_2O_3 apex and includes the compositions of the ternary compounds diopside $\text{CaMgSi}_2\text{O}_6$, grossular $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, and pyrope $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$. Its position in the tetrahedron and its relation to other mineral compounds is shown in fig. 1.

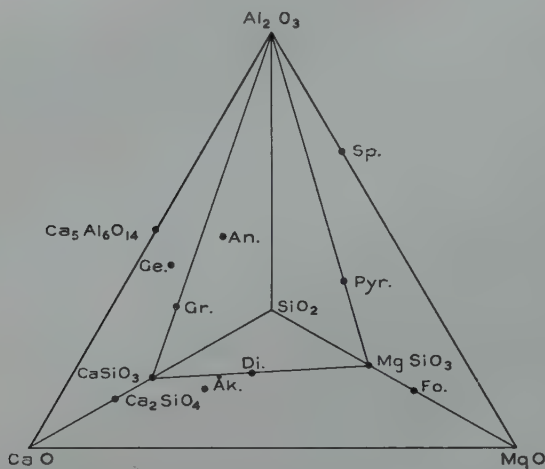
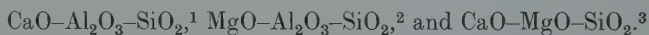


FIG. 1. The quaternary system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ showing the position of the plane $\text{CaSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$ and of the ternary compounds mentioned in the text. Åk, åkermanite; An, anorthite; Di, diopside; Fo, forsterite; Ge, gehlenite; Gr, grossular; Pyr, pyrope; Sp, spinel.

Many of the results on the diopside-clinoenstatite-alumina part of the system were kindly made available by Professor Penkti Eskola of the University of Helsinki, and these have been incorporated. Data on the three boundaries of the section were obtained from the three ternary systems through which they pass:



Experimental. For all the experimental work the standard methods of the Geophysical Laboratory, Washington, were used.⁴ Sources of CaO , MgO , and Al_2O_3 were calcium carbonate, magnesium oxide, and aluminium oxide of analytical reagent quality. Crushed rock-crystal

¹ G. A. Rankin and F. E. Wright, *Amer. Journ. Sci.*, 1915, ser. 4, vol. 39, p. 1.

² G. A. Rankin and H. E. Merwin, *ibid.*, 1918, ser. 4, vol. 45, p. 301.

³ J. B. Ferguson and H. E. Merwin, *ibid.*, 1919, ser. 4, vol. 48, p. 81.

⁴ G. A. Rankin and F. E. Wright, *loc. cit.*

washed in hydrochloric acid was the source of silica. These compounds were mixed in the requisite proportions and fused in platinum crucibles three to five times with intermediate crushings until homogeneous. The final glasses were crystallized by heating at about 1000°C . for several

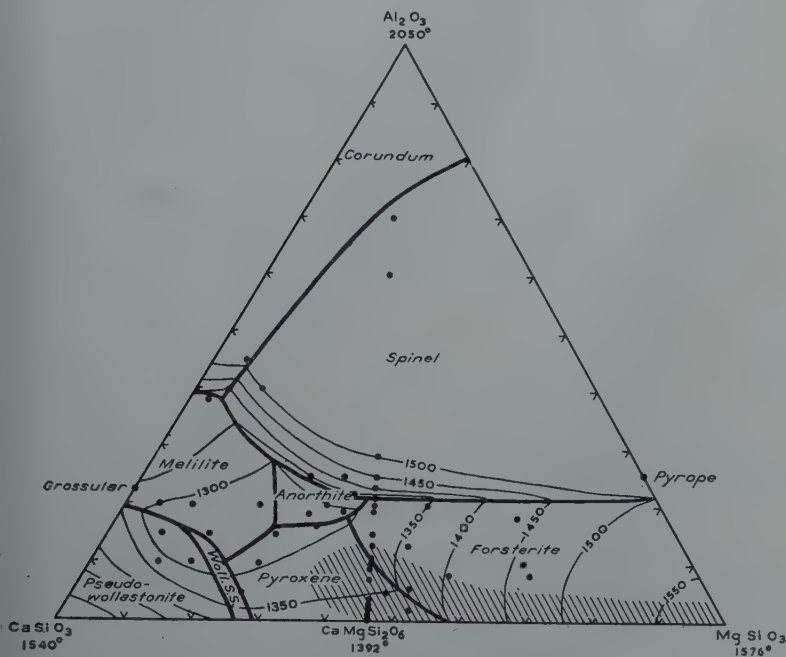


FIG. 2. The section $\text{CaSiO}_3\text{--MgSiO}_3\text{--Al}_2\text{O}_3$ showing primary phase fields, liquidus isotherms, pyroxene solid solutions, and compositions studied.

hours. The resulting finely crystalline material was then examined by the quenching method.

Results. The eight primary phase volumes of corundum, spinel, melilite, anorthite, wollastonite, pseudowollastonite, pyroxene, and forsterite are intersected by the section. All of these phases are well known; their appearance in the quenched charges of this work was as follows: *corundum*, large, thin hexagonal plates; *spinel*, small octahedra; *anorthite*, very thin rhomb-shaped plates, the only crystalline phase in the section with its refractive index lower than that of the embedding glass; *melilite*, rectangular crystals frequently showing square cross-sections; *pseudowollastonite*, large crystals sometimes showing hexagonal cross-sections, high birefringence; *wollastonite*,

poorly formed rounded crystals, refractive index close to that of the embedding glass; *forsterite*, well-formed orthorhombic crystals showing dome faces; *pyroxene*, somewhat oval-shaped crystals with birefringence decreasing with increasing MgSiO_3 and alumina content.

Results of quenching experiments are given in tables I and II. Fig. 2 depicts the primary phase fields and liquidus isotherms derived from the results in tables I and II.

TABLE I. Quenching results along the diopside-alumina join.

Diopside, %	Temp. ° C.	Phases observed.†	Diopside, %	Temp. ° C.	Phases observed.†
99*	1384.5	Gl	85*	1334	Gl
	1384	Gl, Py		1269	Gl, Fo
98*	1379	Gl		1256	Gl, Fo, Py
	1377	Gl, Py		1244	Gl, Py
97*	1370	Gl	83*	1252	Gl, Fo
	1369	Gl, Py		1244	Gl, Py
96*	1363	Gl	81*	1309	Gl
	1361	Gl, Py		1303	Gl, Fo
92-84*	1336	Gl		1242	Gl, Py, Fo?
	1333	Gl, Py		1218	Gl, Py
90-52*	1321	Gl	80	1332	Gl
90	1331	Gl, sm.Py		1291	Gl, Fo
	1313	Gl, Py, Fo	79*	1309	Gl
89*	1325	Gl		1301	Gl, Fo
	1321	Gl, Fo	77*	1350	Gl, Sp
	1300	Gl, Fo	75	1458	Gl
	1291	Gl, Py		1443	Gl, sm.Sp
87*	1333	Gl, sm.Fo		1320	Gl, Sp
	1291	Gl, Fo		1307	Gl, Sp, An
	1283	Gl, Fo, Py	71.24*	1515	Gl
	1275	Gl, Py		1495	Gl, Sp
			40*	1600	Gl, Sp
			30*	1600	Gl, Sp

* Determined by P. Eskola.

† Gl = glass, Py = pyroxene, Fo = forsterite, Sp = spinel, An = anorthite, sm. = small amount of.

Glasses. All the compositions prepared formed glasses on cooling the crucibles in water. Those richer in alumina frequently formed glasses on cooling in air, and occasionally on cooling slowly in the furnace. Refractive indices of the glasses did not vary greatly. They increased with the lime content from approximately 1.58 to nearly 1.63. A diagram of isofracts was published in a previous paper.¹

Discussion. The section behaves as a ternary system only over the

¹ E. R. Segnit, loc. cit.

small areas of the pyroxene, CaSiO_3 , and corundum fields. Over the rest of the area of the section equilibrium is quaternary. Crystallization paths of compositions outside of the solid solution areas must pass out of the section and end at a quaternary invariant point. Points at which three solid phases are in equilibrium with liquid are not invariant points, but are points of the section pierced by quaternary univariant lines. At temperatures well below the solidus the area of the section which behaves as a ternary system is probably larger owing to the stability range of the garnets being reached.

One of the most striking features of the diagram is the great extent of the spinel field. It indicates that spinel can occur as the primary phase in certain compositions containing as little as 2 % MgO . The relatively small field for anorthite suggests that this phase volume will disappear altogether with a further small decrease in silica content of melts outside of the section.

The join diopside-alumina is not a true binary system. At the extreme ends it will act as such, but over the greater part of its length spinel and forsterite are the first phases to crystallize. Under equilibrium conditions mixtures with up to 13 % Al_2O_3 will crystallize as homogeneous pyroxene, this being the limit of solid solution of alumina in that phase.¹ Compositions between 11 and 13 % Al_2O_3 have forsterite as primary phase, which under equilibrium conditions will react with the liquid to form pyroxene as the temperature falls. The final product will be all pyroxene solid solution. Compositions from 13 to 21 % Al_2O_3 also have forsterite as their primary phase; this again reacts with the liquid to form pyroxene, crystallization finishing outside the section. A diagram showing the liquidus and some of the sub-liquidus relations along part of the join is given in fig. 3.

In the low-alumina part of the section is a large solid solution area of alumina in the diopside-clinoenstatite series of pyroxenes (shaded area, fig. 2). Under equilibrium conditions, all compositions within this field will crystallize as homogeneous pyroxene.

This section of the system $\text{CaO--MgO--Al}_2\text{O}_3\text{--SiO}_2$ has a number of petrologic applications. It covers the field of aluminous pyroxenes of the diopside-clinoenstatite series, and contains the compositions of several of the most important minerals of thermally metamorphosed carbonate rocks, notably the assemblage diopside-grossular-wollastonite.

The aluminous pyroxenes of this section have been discussed at some

¹ E. R. Segnit, loc. cit.

TABLE II.

Results of quenching experiments in the section $\text{CaSiO}_3\text{--MgSiO}_3\text{--Al}_2\text{O}_3$.

CaSiO_3 %	MgSiO_3 %	Al_2O_3 %	Temp. ° C.	Phases observed.†
The pyroxene field.				
46.4*	51.6	2.0	1386	Gl
			1381	Gl, Py
48.3	46.7	5.0	1359	Gl
			1346	Gl, Py
			1323	Gl, Py, Fo
			1321	Gl
70.0	25.0	5.0	1310	Gl, sm.Py
			1301	Gl, Sp, Wo
			1279	Gl
			1265	Gl, Py
65.0	25.0	10.0	1239	Gl, Py, Wo
			1265	Gl
			1260	Gl, Py
60.0	25.0	15.0	1257	Gl, Py
53.5	30.1	16.4		
The forsterite field.				
26.7*	69.3	4.0	1480	Gl
			1462	Gl, Fo
44.61*	49.54	5.85	1363	Gl
			1359	Gl, Fo
37.7*	54.3	8.0	1407	Gl
			1403	Gl, Fo
25.6*	66.4	8.0	1471	Gl
			1455	Gl, Fo
25.1*	64.9	10.0	1327	Gl, Fo
			1312	Gl, Fo, Py
			1256	Gl, Fo, Py
41.2*	45.8	13.0	1372	Gl
			1355	Gl, Fo
22.8*	59.2	18.0	1438	Gl
			1430	Gl, Fo
35.0	45.0	20.0	1344	Gl, Fo
The corundum field.				
55.0	5.0	40.0	1406	Gl, sm.Cor
			1381	Gl, Cor, sm.Sp
			1361	Gl, Cor, Sp, An
50.0	5.0	45.0	1520	Gl, Cor
			1464	Gl, Cor
			1423	Gl, Cor, Sp

TABLE II (*continued*).

CaSiO ₃ %	MgSiO ₃ %	Al ₂ O ₃ %	Temp. ° C.	Phases observed.†
The pseudowollastonite field.				
75.0	15.0	10.0	1291	Gl
			1283	Gl, sm. <i>ψ</i> -Wo
			1263	Gl, <i>ψ</i> -Wo
80.0	10.0	10.0	1321	Gl
			1310	Gl, <i>ψ</i> -Wo
77.0	8.0	15.0	1259	Gl
			1249	Gl, <i>ψ</i> -Wo
			1239	Gl, <i>ψ</i> -Wo
			1222	Gl, <i>ψ</i> -Wo, Mel
The anorthite field.				
53.4	27.8	18.8	1270	Gl
			1259	Gl, An
			1183	Gl, An, Py
48.0	33.0	19.0	1289	Gl
			1285	Gl, An
			1269	Gl, An, Fo
50.0	30.0	20.0	1291	Gl, An
			1229	Gl, An, Py
The melilite field.				
70.0	20.0	10.0	1296	Gl
			1291	Gl, sm. Mel
			1288	Gl, Mel, Py
70.0	15.0	15.0	1262	Gl
			1249	Gl, Mel, Wo
60.0	20.0	20.0	1257	Gl
			1244	Gl, Mel
70.0	10.0	20.0	1257	Gl, sm. Mel
			1244	Gl, Mel
75.0	5.0	20.0	1296	Gl, sm. Mel
			1288	Gl, Mel, sm. An
59.0	3.0	38.0	1374	Gl
			1372	Gl, Mel, sm. An
			1366	Gl, Mel, An
The spinel field.				
21.7*	56.3	22.0	1438	Gl
			1426	Gl, Sp
45.0	33.0	22.0	1368	Gl
			1353	Gl, sm. Sp
			1311	Gl, Sp, An
			1285	sm. Gl, Sp, An, Fo
45.0	30.0	25.0	1343	Gl, Sp
50.0	25.0	25.0	1344	Gl, Sp
50.0	10.0	40.0	1450	Gl, Sp

* Determined by P. Eskola.

† Gl = glass, Py = pyroxene, Fo = forsterite, Cor = corundum, Wo = wollastonite, ψ -Wo = pseudowollastonite, An = anorthite, Mel = melilite, Sp = spinel, sm. = small amount of.

length in a previous paper.¹ It is now possible, therefore, to draw certain inferences concerning the occurrence and associations of aluminous diopsides. The diopside-spinel join is on the silica-poor side of the $\text{CaSiO}_3\text{-MgSiO}_3\text{-Al}_2\text{O}_3$ plane and will pass through part of the solid solution volume. This join, however, is not a true binary system. This

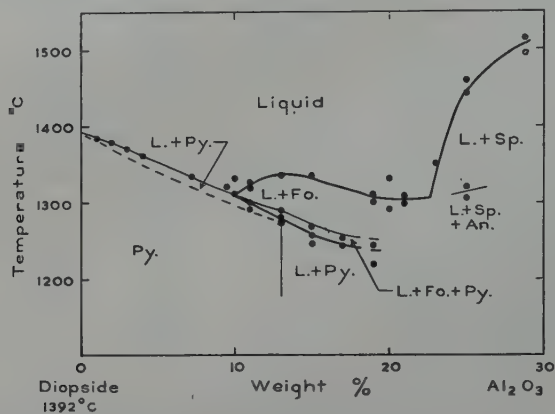


FIG. 3. Some liquidus and sub-liquidus relationships along part of the line diopside-alumina.

is evident from the work of Osborn *et al.*² The join pierces their 15% Al_2O_3 plane of the quaternary system in the forsterite field. Also, the pyroxene and spinel volumes do not appear to touch at any place, so that the pure compounds cannot co-exist with liquid. This is not in agreement with observations on natural rocks, where pyroxene-spinel assemblages are well known. C. E. Tilley,³ for example, has published analyses of aluminous pyroxene and spinel from two diopside-spinel assemblages; the pyroxenes in each case contained over 7% Al_2O_3 . There are two possible explanations of this discrepancy: the fields of stability of the two compounds may come together at sub-solidus temperatures; and in the natural assemblages a small amount of FeO and Fe_2O_3 is present, which may affect the positions of the phase fields. The spinel-diopside join is never very far from the spinel and diopside boundaries when in the forsterite phase volume; it is possible, therefore, that the FeO and Fe_2O_3 (and possibly other constituents) present in natural pyroxene and spinel may shift the phase boundaries enough to

¹ E. R. Segnit, loc. cit.

² E. F. Osborn, R. C. DeVries, K. H. Gee, and H. M. Kraner, loc. cit.

³ C. E. Tilley, *Geol. Mag.*, 1938, vol. 75, p. 81 [M.A. 7-181].

make the join sensibly binary. Assuming that either or both of these explanations hold, any composition on or near this line will have its equilibrium products controlled by a binary system with considerable solid solution at the pyroxene end. The resulting assemblage would therefore be aluminous diopside-spinel with little or no other phases.

On the SiO_2 side of the $\text{CaSiO}_3\text{--MgSiO}_3\text{--Al}_2\text{O}_3$ plane in the region of the diopside-alumina join, compositions close to the binary join anorthite-diopside are encountered. A small amount of silica over that needed for an aluminous diopside can probably be absorbed into the pyroxene structure. That is, the composition is still in the solid solution volume. The join diopside-anorthite, which makes a relatively small angle with the base of the quaternary system, passes through a part of the solid solution volume which takes in pyroxenes with only a low content of Al_2O_3 . Pyroxenes in a diopside-plagioclase assemblage should therefore tend to be less aluminous. The steeper diopside-spinel join on the other hand will pass through a greater distance of the solid solution volume and through a part embracing pyroxenes of much higher Al_2O_3 content. This is in agreement with the opinions expressed by Tilley in connexion with natural pyroxenes. He also points out that the diopside-alumina join lies in the plane diopside-anorthite-spinel, so that diopside-alumina mixtures up to 48.5 % Al_2O_3 may be expressed as a mixture of diopside, anorthite, and spinel. However, spinel could not be expected to appear along this line until the alumina content was rather high. A re-examination of a series of powder photographs of diopside-alumina mixtures taken for the previous paper showed no spinel lines amongst those of diopside and anorthite up to mixtures containing 30 % Al_2O_3 , the maximum photographed. Small amounts of spinel are probably present at this stage, but not in sufficient amount to be recorded on a powder photograph.

The composition of grossular appears on the $\text{CaSiO}_3\text{--Al}_2\text{O}_3$ side of the section (figs. 1 and 2). For the conditions under which grossular is stable there would have to be a join diopside-grossular, and the composition triangle diopside-grossular-wollastonite. Both these assemblages are well known in thermally metamorphosed carbonate rocks. The temperature and pressure conditions under which this equilibrium can be reached in the diagram is not definitely known. Yoder¹ has recently investigated the stability relations of grossular, and his work indicates that low temperatures (of the order of 750° C. and lower for hydrogrossular) are probably more important than high pressures for the formation of this

¹ H. S. Yoder, *Journ. Geol.*, Chicago, 1950, vol. 58, p. 221 [M.A. 11-197].

garnet. High pressures, however, would probably assist its formation. The assemblage diopside-grossular-wollastonite will therefore be represented by a sub-solidus composition triangle in the section $\text{CaSiO}_3\text{--MgSiO}_3\text{--Al}_2\text{O}_3$. The join diopside-grossular passes through part of the solid solution field of diopside, so that a small area of solid solution exists in the diopside-grossular-wollastonite triangle. The maximum Al_2O_3 content of any pyroxene in this triangle is 5 %, so that, in general, we would not expect diopsides of these parageneses to contain much alumina. This appears to be commonly the case. A diopside separated from a diopside-grossular rock from Norway (Dept. Min. Petr. Cambridge, Spec. 26010), for example, analysed: SiO_2 53.76, Al_2O_3 1.46, Fe_2O_3 0.90, FeO 2.12, CaO 25.69, MgO 15.92, total 99.85. In contrast to this it must, however, be noted that analyses of high-alumina diopsidic pyroxenes associated with garnet have been published.¹

The composition of the magnesian garnet pyrope occurs on the $\text{MgSiO}_3\text{--Al}_2\text{O}_3$ side of the diagram. The diopside-pyrope join passes through a large part of the solid solution area of diopside, so that it could be possible for the omphacites of eclogites to contain some of their alumina in the tetrahedral groups. Alderman² records six analyses of omphacites from eclogites. These pyroxenes contain from 1.13 to 7.01 % of alkalis, thus allowing most of the alumina content to replace (Mg,Fe) in the Y group. In two of the analyses, however, there is still a surplus of a third to a fifth of the total alumina (amounting to approximately 2 % Al_2O_3 in the mineral) which must be replacing silicon in the tetrahedral groups.

Acknowledgements.—The author desires to record his appreciation of the assistance given in this work by Professor C. E. Tilley, and of the helpful discussion with Professor P. Eskola, as well as his permission to use some of his results in this paper.

¹ J. Kratzert, *Centr. Min.*, 1922, p. 561.

² A. R. Alderman, *Quart. Journ. Geol. Soc.*, 1936, vol. 42, p. 488.

Some new occurrences of gonnardite.

(With Plate X.)

By H. MEIXNER, Ph.D.,

Bergdirektion, Hüttenberg, Carinthia, Austria,

M. H. HEY, M.A., D.Sc., and A. A. MOSS, B.Sc., Ph.D., F.S.A.,

Department of Mineralogy, British Museum.

[Read 3 November 1955.]

Summary.—This zeolite, hitherto recorded only from Chaux de Bergonne, France, has been found as zoned spherules with thomsonite (var. faroelite), on specimens from Aci Castello and Aci Trezza, Sicily, and Capo di Bove, Rome, from Weilberg, Rhineland, and from Klösch, Styria. Three chemical analyses confirm previous results; optical data suggest some variation in composition within a spherule. There is a striking resemblance between X-ray fibre photographs of gonnardite and of thomsonite, and between X-ray powder photographs of gonnardite and of natrolite. The Klösch occurrence, where the gonnardite is accompanied by phillipsite, is described in detail.

DURING a routine examination of a number of zeolites recently acquired by the British Museum, specimens from Aci Castello and Aci Trezza, Catania, Sicily, labelled mesolite, or phillipsite, were found to have optical properties substantially different from those of either mesolite or phillipsite; the refractive indices were near those of mesolite, but the birefringence, although weak, was too high for mesolite, and the straight extinction of the fibres precluded their being a fibrous phillipsite. X-ray powder photographs closely resembled those of natrolite, but more careful examination showed that the mineral is gonnardite, a zeolite hitherto only recorded from Chaux de Bergonne, Gignat, Puy-de-Dôme, France, and this identification is confirmed by chemical analysis and by a more detailed optical study. On the three Sicilian specimens, the gonnardite forms white spherules, up to $\frac{1}{2}$ inch in diameter, on a vesicular basalt, and is accompanied by needles of calcite, small drusy spherules of columnar phillipsite, and chabazite crystallized in the phacolite habit. On re-examination of a number of other fibrous zeolites gonnardite was found as a few white spherules, up to $\frac{1}{2}$ inch in diameter, alone in a cavity in leucite-tephrite from Capo di Bove, Rome (B.M. 82805; pl. X,E), and also accompanying very fine cruciform twins

of phillipsite in a cavity in basalt from Weilberg, Rhineland (B.M. 1908, 308(20)). About the same time, one of us (H. M.) observed a zeolite in the basalt of Klösch, Styria, which gave X-ray powder photographs closely resembling those of natrolite, but had too high a refractive index. Comparison with type material from Chaux de Bergonne, presented by Prof. A. Lacroix (B.M. 1930, 166), shows that the Klösch zeolite, too, is gonnardite.

With more adequate supplies of material available, three new semi-micro chemical analyses of gonnardite have been made (table I); these

TABLE I. Chemical and optical data for gonnardite.

	A.	B.	C.	D.	E.		A*.	B*.	C*.	D*.
SiO ₂	42.80	43.20	42.75	41.85	42.3	Si ...	11.7	11.8	11.7	11.3
Al ₂ O ₃	28.15	27.90	27.36	27.02	28.1	Al ...	9.1	9.0	8.8	8.6
CaO	4.26	3.61	7.77	9.29	10.0	Ca ...	1.2	1.0	2.3	2.7
Na ₂ O	12.65	13.16	8.15	7.25	6.7	Na ...	6.7	7.0	4.3	3.8
K ₂ O	0.13	tr.	0.15	n.d.	n.d.	K ...	0.04	tr.	0.05	—
H ₂ O	11.85	11.74	13.44	14.37	14.1	O ...	41.6	41.5	41.0	40.2
Sum	99.84	99.61	99.62	99.78	101.2					
D ₄ ²⁰	2.28†	2.27†	2.27†	2.26‡	2.26- 2.36	H ₂ O ...	10.8	10.7	12.2	13.0
α _§	1.498	1.497	1.506	1.506	—	(Si,Al)	20.8	20.8	20.5	19.9
γ _§	1.502	1.499	1.508	1.508	—	(Ca,Na,K)	7.9	8.0	6.7	6.5
Elongn.	β	+	—	—	+					

A. Klösch, Styria. B.M. 1955, 313.

B. Aci Trezza, Sicily. B.M. 1954, 184.

C. Aci Castello, Sicily. B.M. 1954, 45.

D. Chaux de Bergonne, France. B.M. 83037. Anal. M. H. Hey (1932).

E. Chaux de Bergonne, France. Anal. F. Pisani (F. Gonnard, 1871); optical data by A. Lacroix (1896).

A*—D*. Empirical and semi-empirical unit-cell contents, using the cell-dimensions determined on specimen D (Hey, 1932). The assessed probable error of ± 0.05 for the cell-sides leads to a probable error of approximately $\pm 3\%$ in the cell contents (1.2 in O); it is probably an underestimate.

† ± 0.01 .

‡ ± 0.02 .

§ ± 0.002 to 0.003 .

confirm the unit-cell formula found earlier, [(Ca, Na)₆₋₈(Si,Al)₂₀O₄₀. 12H₂O], with Al near 9 (M. H. Hey, 1932). The unit cell is near that of thomsonite, except for the halving of the *c*-dimension, and the composition is only a little more silica-rich than some faroelites. It is interesting to note the very small percentage of potassium in all the analysed specimens, despite the fact that all are accompanied by phillipsite, of which potassium is an essential constituent; the formation of a potassium-natrolite by base-exchange shows clearly that potassium can enter most zeolite structures but the strong preference for sodium and calcium has been noticed before.

X-ray rotation photographs of gonnardite resemble those of thomsonite, especially if the exposure has been too short to bring out the weak odd layer-lines of thomsonite, but powder photographs of the two

TABLE II. X-ray powder data for gonnardite (B.M. 1908, 272, Chaux de Bergonne, France) and natrolite (B.M. 1914, 769, Snake Hill, Hudson County, New Jersey). Camera diameter 6 cm. Cu- $K\alpha$ radiation. In the intensities columns, the three strongest lines are numbered.

Gonnardite.		Natrolite.		Gonnardite.		Natrolite.	
<i>d.</i>	<i>I.</i>	<i>d.</i>	<i>I.</i>	<i>d.</i>	<i>I.</i>	<i>d.</i>	<i>I.</i>
6.70	s	6.53	s	1.323	mw	1.627	mw
5.93	vs 2	5.87	vs 2	1.291	vw	1.600	mw
5.25	w	4.64	m	1.262	vvw ?	1.571	vw
4.74	ms	4.36	vs 3	1.237	mw	1.530	mw
4.44	s 3	4.14	ms	1.202	vw	1.510	vvw
4.22	mw	3.90	vvw	1.178	vvw	1.485	vvw
3.69	vw	3.64	vvw	1.157	vw	1.462	m
3.52	vvw	3.17	ms	1.129	vvw	1.431	vvw
3.23	ms	3.11	m	1.095	vw	1.415	w
3.12	m	2.95	m	1.080	vvw	1.386	mw
2.92	vvs 1	2.86	vvs 1	1.069	vw	1.367	vw
2.61	m	2.75	vvw	1.060	vw	1.341	vw
2.48	m	2.67	vvw	1.048	vvw	1.324	w
2.36	w	2.58	m	1.039	vvw	1.306	mw
2.33	vvw	2.52	vvw	1.032	vvw	1.290	vvw
2.28	w	2.45	m			1.273	vw
2.22	m	2.41	m			1.261	vvw
2.16	vvw	2.33	mw			1.238	vvw
2.12	vvwb	2.26	w			1.218	mw
2.07	w	2.19	m			1.193	w
1.98	wb	2.12	vvw			1.178	vvwb
1.895	mw	2.06	w			1.160	vvwb
1.851	w	2.02	vvw			1.142	vw
1.818	mw	1.96	w			1.130	vw
1.759	mw b	1.93	vvw			1.109	vvwb
1.697	w	1.876	mw			1.091	vw
1.647	m	1.831	vvw			1.080	vvw
1.607	w	1.799	m			1.060	vw
1.548	wb	1.754	w			1.050	vvw
1.486	mw	1.728	mw			1.037	vvw
1.442	w	1.700	w			1.022	w
1.398	wb	1.676	vw				
1.348	vw	1.647	w				

minerals are readily distinguished. On the other hand, while rotation photographs of gonnardite and natrolite are quite distinct, their powder photographs are remarkably similar and can be confused (pl. X, B, c); the most notable differences are in the region from $d = 2.00$ to $d = 1.30$ Å. Optically, gonnardite is distinguished from other fibrous zeolites giving

straight extinction by its refractive index and birefringence; the latter is about 0.002 to 0.004, noticeably higher than that of mesolite (< 0.001), while its refractive index, ranging from about 1.497 to 1.507, is higher than that of natrolite (γ 1.497), overlaps that of mesolite (1.505), and is lower than that of the most siliceous faroelite so far recorded (α 1.511).



FIG. 1. Zones of varying birefringence and optical sign in gonnardite from Aci Castello, Sicily (B.M. 1954, 130).

Mordenite, which has a rather similar birefringence, has a much lower refractive index (γ 1.480); stellerite, a variety of stilbite, has practically straight extinction, but a lower refractive index (γ 1.492) and higher birefringence (0.007).

A notable characteristic of the Sicilian gonnardite specimens that we have studied is the zonal structure of the spherules in which the mineral always crystallizes. As indicated in fig. 1, a small splinter under crossed nicols often shows several zones, some with positive elongation, some with negative, and all

grading into one another; though owing to the finely fibrous structure it is not possible to be sure whether this gradation occurs within the individual fibres or is due to variations in the length and position of the several zones from fibre to fibre. X-ray photographs of fragments from different zones (taken from a specimen with a less complex zonal structure than that figured) show no differences, and all the zones are gonnardite: presumably there are differences in chemical composition between the positive, negative, and isotropic zones, but it was not possible to obtain enough material to analyse these zones separately. Some of the zones are visible to the naked eye in ordinary light as more glassy or transparent zones in the white surface of a broken spherule; this may be due to reduced scattering in the more nearly isotropic material.

All the specimens were examined optically (compare table I); four from Chaux de Bergonne showed very little variation in optics; about 50 from Klöch showed appreciable variations in the refractive index, α' , in one specimen being as high as 1.503, while the analysed specimen had the lowest refractive indices of any examined; a specimen from Aci Castello (B.M. 1954, 130) gave the most complex zonal structure, and resembled the Aci Trezza specimen in refractive indices.

The zeolites of the Klösch basalt (H. M.).

All the new occurrences of gonnardite except that at Klösch are only known from a limited number of small hand-specimens, the precise provenance of which has not been established; much of the Klösch material, on the other hand, was collected by one of the authors (H. M.) and a full description of its occurrence is appended.¹

Five kilometres north of Halbenrain near Radkersburg, on the Austro-Yugoslav frontier, lies the village of Klösch, and in the 'Klöcher Klause', about 350 metres north of the church, a series of basalt quarries, in which the basalt shows pronounced columnar jointing, have been opened. A detailed examination by K. Schoklitsch (1932) of this basalt, which was classified as nepheline-basanite by A. Sigmund (1895), has shown that, according to the Niggli system, its composition lies between that of the theralitic and the theralitic-gabbro magmas, and A. Winkler (1951) has given reasons for regarding the volcanic activity in these rocks as having occurred in lower Upper Pliocene times (Dacian stage), although it had long been regarded as of late Pannonic age.

In the first quarry north of Klösch, a column of basalt 10 metres thick was exposed, which was overlain by a vesicular basalt. In this basalt A. Hödl (1942) reported calcite crystals and large (up to 4 cm. long) crystals of aragonite with well-developed faces, together with smaller crystals (a few mm. across) of nepheline and analcime, which had grown out of the rock into the vesicles. In 1951, on the floor of the north corner of the same quarry, some particularly fine specimens of zeolites were collected, the best being crystals of phillipsite, and spherulites of gonnardite 1 cm. in diameter. Since then, other zeolites have been found in the same vicinity; according to P. Paulitsch (1952), chabazite occurs as colourless crystals 5 mm. in length all with $\{10\bar{1}1\}$ faces and sometimes twinned on (0001), and accompanied by scaly stilbite; Paulitsch has also reported (private communication) that some unusually well-developed crystals of thaumasite were also present; K. Kontrus (1952) has also described occurrences of phillipsite together with chabazite in the lens-shaped phacolite habit with the forms $\{10\bar{1}1\}$ and $\{01\bar{1}2\}$. These zeolites of Klösch have all formed in the vesicular hollows, which rarely attain the size of the hand. Small vesicles are occasionally filled completely by hydrothermal minerals, but drusy deposits are the most common. The oldest mineral in the vesicles is

¹ Our thanks are due to Herr W. Philippek of Graz, who first collected these associated zeolites at Klösch, for providing many of the specimens examined during the course of this investigation.

calcite, often occurring alone and frequently forming the base of the zeolites. The crystals are almost always very small, measuring only a fraction of a mm., often in comb-like aggregates but sometimes botryoidal.

Phillipsite¹ is the commonest zeolite and is older than the gonnardite. Occasionally it occurs as transparent, pseudo-tetragonal, prismatic interpenetration twins (Dana,² fig. 2); but it is usually found as translucent complex twins (Dana, figs. 3 and 4, and pl. X, D of this paper). The re-entrant angles are often absent, resulting in pseudo-rhombic-dodecahedra. The phillipsite specimens from Klösch are the equal of those from the best localities.

The more simple twins might, from their appearance, be harmotome, but, according to G. Kalb and H. Klotzsch (1943), the pseudo-cubic multiple twins of phillipsite are characteristic.³ Phillipsite has been found by A. Köhler (1932) in the Neuhaus (Burgenland) basalt, but the mineral from the basalt at Weitendorf (near Wildon, Styria) that was reported as phillipsite by A. Sigmund (1924, 1926) has been shown by F. Machatschki (1926) to be harmotome (see also H. Heritsch, 1936).

Chabazite was present in only one specimen as a lenticular crystal nearly 2 mm. long. Calcite crystals formed the base and much phillipsite was present. On one specimen some colourless spherules of a mineral reminiscent of hyalite were found, together with phillipsite and small calcite crystals. The mineral was anisotropic, fibrous, and had straight extinction, with positive and negative elongation and gave β about 1.520, and $\gamma - \beta > \beta - \alpha$, showing it to be thomsonite.

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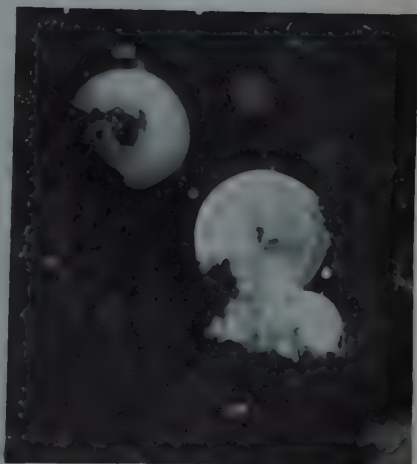
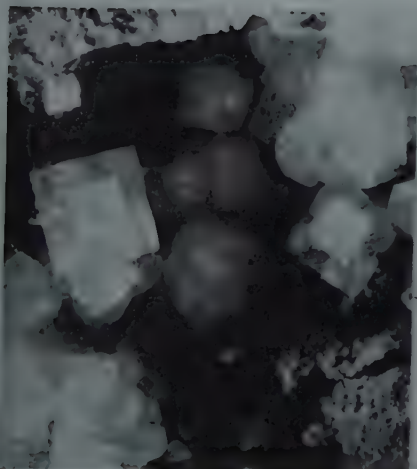
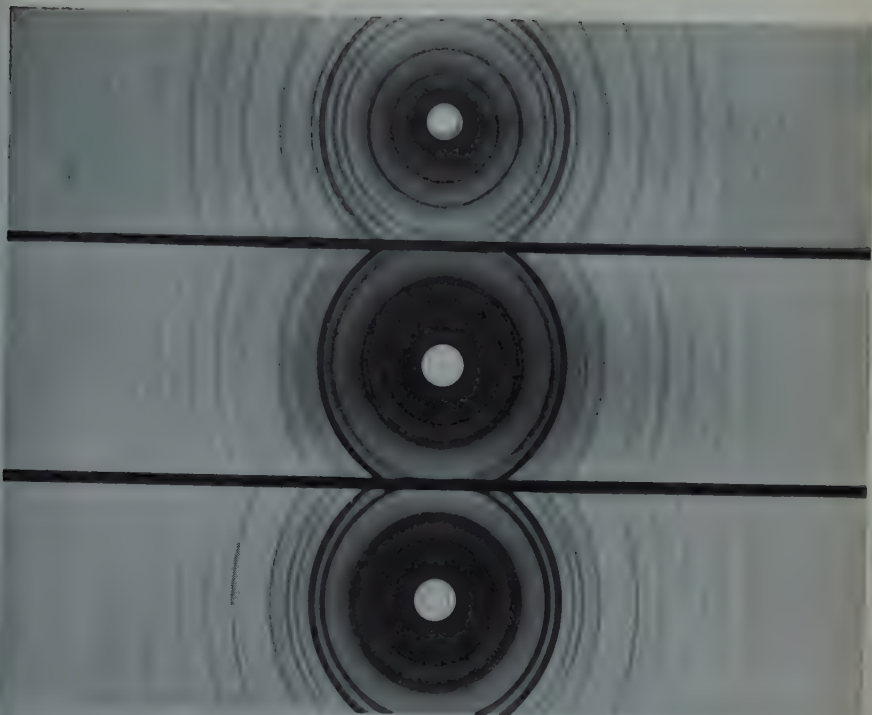
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¹ Identified by refractive index (< 1.501) and density (2.216).

² *Syst. Min.*, 6th edn (1892), p. 579.

³ As a result of a detailed study of vicinal forms, these authors regard phillipsite (and harmotome) as orthorhombic and not monoclinic.



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EXPLANATION OF PLATE X.

- A to C, X-ray powder photographs, 6 cm. camera, Cu- $K\alpha$ radiation.
- A. Thomsonite, Old Kilpatrick, Dumbartonshire.
- B. Gonnardite, Chaux de Bergonne, France.
- C. Natrolite, Snake Hill, New Jersey.
- D. Phillipsite, multiple twins in cavity of basalt, Klösch, Styria. Approx. $\times 2$.
Photo. by K. Kontrus.
- E. Gonnardite, zoned spherule in leucite-tephrite from Capo di Bove, Rome (B.M. 82805). Approx. natural size.
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An effect of depth of focus on micrometric analysis.

By R. B. ELLIOTT, B.Sc., Ph.D., F.G.S.

Department of Geology, The University, Nottingham.

[Taken as read 7 June 1956.]

Summary.—When using many patterns of integrating stage the depth of focus is so great that it is not possible to distinguish between the upper and lower surfaces of a thin section; this may introduce serious errors into micrometric analyses. A procedure to meet this difficulty is suggested.

THE classic method of micrometric analysis of Delesse required that all measurements should be made on a single plane in a rock and in modern analysis the plane frequently selected is the surface of a thin section (Chayes, 1953, 1954). It is here suggested that under certain conditions of micrometric analysis no such single surface can be differentiated and instead both upper and lower surfaces of a thin section may be in simultaneous focus. When this is so and the analyst is unaware of the fact errors may occur. To eliminate errors from this source measurements can be made on a plane, selected between crossed nicols if necessary, in the centre of the slide. Areas measured on this plane are mean areas and, as such, are directly proportional to volumes.

The reason why no single surface can be differentiated under certain conditions of micrometric analysis is due to the fundamental deficiencies of the optical system of the microscope, whereby a depth of focus, which varies with the numerical aperture, is introduced.

The objectives commonly used in measurement are those of focal lengths about $\frac{2}{3}$ inch, $\frac{1}{3}$ inch, and $\frac{1}{6}$ inch, with numerical apertures of approximately 0.25, 0.45, and 0.65, respectively. On the Leitz stage these objectives give the following performance: The 0.25 N.A. objective gives a clear picture of the full thickness of the slide with both upper and lower surfaces sharply in focus at the same time. The 0.45 N.A. objective allows discrimination of the two surfaces of the slide where the crystal margins are well defined; where the crystal margins are irregular the separation of the two surfaces is not easily obtained and requires both time and care, since a considerable depth of the slide is visible. The 0.65 N.A. objective distinguishes the two surfaces of the slide and has shallow depth of focus.

This is at first sight surprising for the quoted depths of focus for these objectives are of the order of 0.008 mm., 0.0024 mm., and 0.001 mm., all very much less than the thickness of a thin section, so that all might be expected to be capable of focusing sharply on one surface to the exclusion of the other, and to have a shallow depth of focus. The greatly increased depth of focus found in practice is largely due to the conditions under which the objectives operate when used to measure slices on the Leitz integrating stage. This stage is mounted on top of the microscope stage in such a way that the thin section is raised almost an inch above its normal position. The substage condensers cannot be raised to their usual position in relation to the slide and in consequence the objectives and condensers cannot be matched. The high-power condenser cannot be used at all at the increased distance for it gives very inferior illumination and it is necessary to use the low-power condenser of N.A. = 0.22. This gives a satisfactory amount of light but its pencil of rays probably has an aperture, at the increased distance, of about 0.10. (This is a guess on my part but since the distance between condenser and object has been approximately doubled the aperture will be approximately halved.) An objective of N.A. = 0.25 working in conjunction with a condenser of N.A. = 0.10 has an effective N.A. of 0.18. Similarly, objectives of 0.45 N.A. and 0.65 N.A. working with the same condenser will have effective apertures of 0.28 and 0.38. This diminution in aperture increases the depth of focus.

The quoted depth of focus of an objective, df , is calculated from the formula:

$$df = \text{Allowed difference of path to produce no loss of definition} / n \sin^2 U / 2$$

where n is the refractive index of the medium between object and objective and U is half of the full cone of light entering the objective. The allowed difference of path is usually written as $\lambda/4$, where λ is the wave-length of light used, but it may be greater than this for Rayleigh (1896) states that up to $\lambda/2$ path-difference there is no perceptible loss of definition. Substitution of $\lambda/2$ for $\lambda/4$ in the formula doubles the depth of focus.

The depth of focus based on $\lambda/2$ and the reduced apertures are as follows: 0.25 N.A. objective = 0.031 mm.; 0.45 N.A. objective = 0.013 mm.; 0.65 N.A. objective = 0.007 mm.

These figures are computed as distinct from being measured and so are the minimum depths of focus that can be attained. Any factors which serve to decrease the numerical aperture, such as incorrect

thickness of coverslip, stopped-down light, or imperfections in the lens, will serve to increase the depth of focus further. The conclusion to be drawn from the figures is that the 0.25 N.A. objective can focus the full thickness of the section at one time; the 0.45 N.A. objective about half the thickness of the section, and the 0.65 N.A. objective about a quarter of the thickness of the section. This is in agreement with practice.

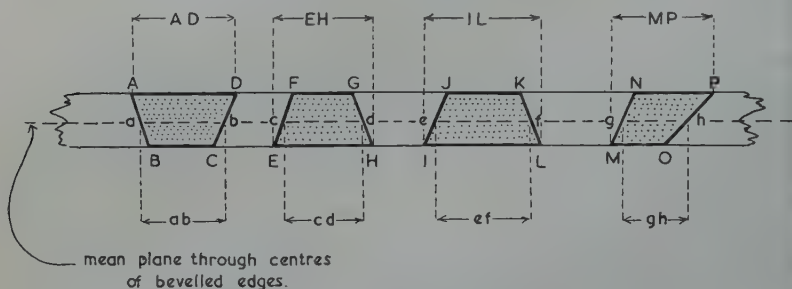


FIG. 1. Cross-section of thin section to show the different grain margins which may be selected for measurement. (a) upper surface, $AD + FG + JK + NP + \dots$; these will give correct mineral ratios. (b), lower surface, $BC + EH + IL + MO + \dots$; these will give correct mineral ratios. (c) $AD + EH + IL + MP + \dots$; these are selected by eye when the whole thickness of the slide is in focus; the error is the superposition error. (d) $ab + cd + ef + gh + \dots$; these are measured from the centres of bevels and give the correct mineral ratios.

Within the depths of focus as established above there is no means of differentiating one plane from another since with monocular microscope vision there is neither stereoscopic differentiation nor aid from perspective, so that all objects in focus are seen to lie in the same plane. Where some considerable depth of focus exists, to accept measurements as those of a single plane is to accept illusion.

These considerations are important when minerals of contrasted relief lie side by side for it is my belief that the eye accepts the maximum diameter, within the depth of focus, of high-relief minerals with inclined margins; and since the horizons of the maxima vary from grain to grain any measurements are effectively taken on more than one plane. When mineral boundaries are inclined, therefore, there is a distinct possibility of superposition error (fig. 1). If the conditions of the analysis allow one to identify, with certainty, that edge of the bevel which intersects the surface of the slide the ordinary procedure can be used, but if there is liable to be any doubt about which is top and which bottom it is possible to eliminate or diminish the error of measurement by measuring,

between crossed nicols if necessary, from the centre of one bevelled edge of a grain to the centre of the other. The centres of the bevels will, on the average, be in the centre of the slice and if all measurements are taken on them they will all be made on a plane—a mean plane—and the result will be more accurate than if they were made on a number of planes in the belief that they were one.

Areas measured from the centres of bevels constitute true mean areas of the several minerals in the slide and, as such, are directly proportional to volumes since $vol. = \text{mean area} \times \delta x$, where δx is the thickness of the slide.

The conclusions are that measurements from the centres of bevels are measurements on a plane, that volumes are proportional to areas measured in this way, and that the measurements constitute a direct measurement of volume. This is certainly not the theory of Delesse but it is nevertheless valid in those instances where a considerable depth of focus exists and where the majority of the grains are greater in size than the thickness of the slice.

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The Holmes effect and the lower limit of modal analysis.

By F. CHAYES.

Geophysical Laboratory, Carnegie Institution of Washington,
Washington, D.C., U.S.A.

[Taken as read 7 June 1956.]

Summary.—Thin-section analysis is essentially an areal measurement, the measurement area usually being the upper surface of the section. If transmitted light is used for the measurement, the apparent areas of opaque grains will in general be somewhat larger than their true areas on the measurement surface. For strictly spherical opaque particles in a transparent matrix the expected excess of apparent over true area is shown to be $(\pi r^2 k)/(2r + k)$ where r is the spherical radius and k is the thickness of the thin section. A table shows the relation between true and apparent area as a function of r/k .

A HOLMES¹ seems to have been the first to note the bias involved in measuring areas of opaque grains in a transparent medium by means of transmitted light. The apparent area of the opaque grain will always be that of its maximum cross-section in the slide, whereas one should be measuring only its 'true' area, e.g. its area at the *surface* of the thin section. Thus in general one will overestimate the relative area of opaque granules on the measurement surface.

For particle shapes of low symmetry the size of the Holmes bias is rather troublesome to calculate. This is true also for highly symmetrical shapes oriented in such a way that the symmetry cannot be utilized. For spherical particles, however, the calculation is straightforward, though somewhat tedious. It is worth carrying through as an indication of the general order of magnitude of the effect for particle shapes of lower symmetry.

A sphere of radius greater than the thickness of the thin section ($r > k$) is shown in fig. 1; the observer is situated somewhere along the positive region and the light source along the negative region of the Y-axis. The distance of the measurement surface (the upper surface of the thin section) from the base of the sphere is given by y , and an opaque area will appear in the field of vision whenever $0 < y < (2r + k)$. For $y \leq r$ the apparent opaque area will be identical with the true one. In the

¹ Petrographic methods and calculations. Thomas Murby and Co., London 1920, p. 317.

region $r \leq y \leq (r+k)$ the apparent area will be constant and equal to the area of the equatorial plane, while the true area, the one the observer should be measuring, decreases steadily as $y \rightarrow (r+k)$. In the region $(r+k) \leq y \leq 2r$ both the true and the apparent areas decrease steadily as $y \rightarrow 2r$, but they do so at different rates and the apparent area is

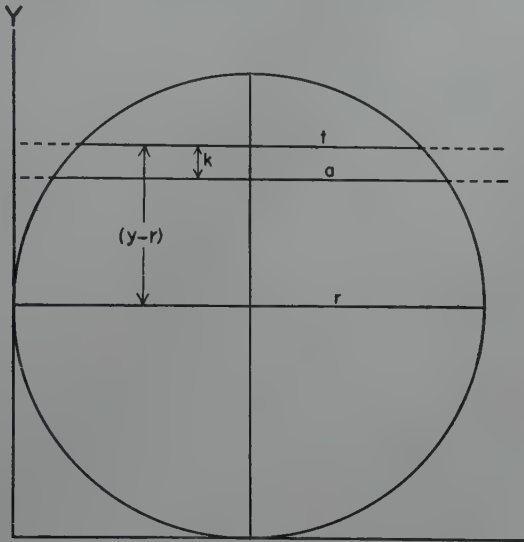


FIG. 1. Thin section of thickness k cutting opaque spherical particle of radius r . The true opaque area at the measurement surface is a circle of radius t ; the apparent opaque area is a circle of radius a .

always larger than the true. Finally, in the region $2r \leq y \leq (2r+k)$, the true area is zero—the sphere does not intersect the measurement surface of the thin section—but the apparent area persists until $y = (2r+k)$, at which point it vanishes. Thus at any y value in the region $0 < y < (2r+k)$ the apparent area is never less than the true, and in the region $r < y < (2r+k)$ it is always larger. Areal measurements made in transmitted light will inevitably be subject to a positive bias and our problem is to estimate the size of this bias. In order to do so we first find the expected or average values for the true and apparent opaque areas. The bias is simply the difference between the two.

Our interest is only with those sections of the sphere in which the apparent area is greater than zero; this will be true of all sections in the region $0 < y < (2r+k)$ and only of such sections. We therefore specify that elevations of measurement areas above the base of the sphere are

to be chosen simply at random, but with the limitation $0 \leq h \leq (2r+k)$, so that the probability that some particular elevation, y , is equal to or less than any arbitrary value, h , is simply $Pr\{0 < y \leq h\} = h/(2r+k)$. The cumulative frequency is accordingly

$$F(h) = \frac{1}{2r+k} \int_0^h dy \quad (1)$$

which is clearly equal to unity when $h = (2r+k)$.

Now the area of any particular circular section at the measurement surface will be:

$$\left. \begin{aligned} A_t &= \pi\{r^2 - (r-y)^2\} = \pi\{r^2 - (y-r)^2\} = \pi(2ry - y^2) \\ \text{in the region } 0 &\leq y \leq 2r, \\ \text{and } A_t &= 0 \text{ in the region } 2r \leq y \leq (2r+k) \end{aligned} \right\} \quad (2)$$

From equations (1) and (2) we have that the expected value or long-range average for the true area is

$$E(A_t) = \frac{\pi}{2r+k} \int_0^{2r} (2ry - y^2) dy = \frac{4\pi r^3}{3(2r+k)}. \quad (3)$$

The apparent area will be

$$\pi(2ry - y^2) \text{ if } 0 \leq y \leq r, \quad \pi r^2 \text{ if } r \leq y \leq (r+k),$$

and

$$\pi\{r^2 - (y-r-k)^2\} = \pi\{2r(y-k) - (y-k)^2\} \text{ if } (r+k) \leq y \leq (2r+k).$$

Hence the expected value of the apparent area will be

$$\begin{aligned} E(A_a) &= \frac{\pi}{2r+k} \int_0^r (2ry - y^2) dy + \frac{\pi r^2}{2r+k} \int_r^{r+k} dy + \\ &+ \frac{\pi}{2r+k} \int_{r+k}^{2r+k} \{2r(y-k) - (y-k)^2\} dy = \frac{4\pi r^3}{3(2r+k)} + \frac{\pi r^2 k}{2r+k}. \end{aligned} \quad (4)$$

The bias, or expected excess of apparent area over true, obtained by subtracting eq. (3) from eq. (4), is $B = E(A_a) - E(A_t) = \pi r^2 k / (2r+k)$. The apparent area will be $E(A_a)/E(A_t)$ times the true one, so that in the rather special case in which a correction would be justified the proper procedure would be to multiply the observed value by

$$C = E(A_t)/E(A_a) = 4r/(4r+3k).$$

Although the figure illustrates only the case in which $r > k$, it can readily be shown that the proof holds also for $r < k$. We are thus in a position to calculate the appropriate correction factor, C , for any ratio of spherical radius to thin-section thickness. Table I shows C for selected

TABLE I. Correction factors for cross-section areas of opaque spheres in a transparent matrix, measured in transmitted light. r/k = ratio of spherical radius (r) to section thickness (k); 'correction' factor $C = 4r/(4r + 3k)$.

r (mm.) for $k = 0.03$ mm.			r (mm.) for $k = 0.03$ mm.		
r/k .		C .	r/k .		C .
200	6.0	0.996	2	0.06	0.727
100	3.0	0.993	1	0.03	0.571
50	1.5	0.985	0.50	0.015	0.400
33	1.0	0.978	0.33	0.010	0.308
20	0.6	0.964	0.25	0.0075	0.250
10	0.3	0.930	0.20	0.0060	0.210
5	0.15	0.897	0.10	0.0030	0.118
4	0.12	0.842	0.067	0.0020	0.082
3	0.09	0.800	0.033	0.0010	0.043

values of r/k in the range $200 \geq r/k \geq 0.033$. The second column of the table shows r in millimetres for $k = 0.03$ mm., the standard section thickness used in most petrographic laboratories. The third column of the table, of course, applies strictly only to opaque spherical particles in a transparent matrix.

The Holmes effect is not likely to be of much importance if opaque constituents are present only in small amount, and in grains of reasonable size, as in most common rocks. Whenever the amount of opaque material is large or the 'grain size' of the opaque particles is small, however, the situation is very different. Estimates of magnetite dust in plagioclase, for instance, could easily be absurdly high. If the radius were 0.015 mm., a value not unreasonably small, one would overestimate the dust by a factor of 2.5. For a radius of 0.01 mm. the 'observed' amount would be high by a factor of 3.25. And for a radius of 0.003 mm., one-tenth the thickness of the slide, the true opaque area would be a little less than one-eighth of the apparent area.

Similar difficulties may be anticipated in the analysis of fine-grained sediments, such as black shales, which contain considerable amounts of finely divided organic or other opaque material. Under such circumstances microscopic analyses may be internally consistent—and hence useful for many geological purposes—provided specimens being compared with each other do not differ materially in grain size. It is not to be expected, however, that the results will tell much about the modal

compositions of the parent materials. In general they will overestimate the amount of opaque material; even a good guess as to the size of the overestimate, however, will require more information than is ordinarily available and perhaps more than can be obtained.

R. B. Elliott¹ has argued that something similar to the Holmes effect may be generated by the juxtaposition of transparent minerals differing greatly in refractive index. Although relief is strictly a property of the contacts between grains, we do generally identify it with the mineral whose index differs more from that of the mounting medium. Accordingly, if we are unable to locate the intersections of grain contacts with some specific measurement plane—usually the upper surface of the thin section—our measurements may well be subject to the Holmes effect, even though all the constituents involved are transparent.

Even when index difference is not enough to produce strong relief, inability to locate the measurement surface may introduce large constant errors. Most of the members of a swarm of perthitic albite blebs, for instance, may be below the surface of the thin section, yet all may show the appropriate Becke line against the host, and differences in birefringence or extinction will not be obscured by the fact that many of the blebs are partly or entirely beneath the measurement surface.

Provided there is no tendency for some particular transparent mineral to mantle the opaque granules, the Holmes effect could be overcome by measuring the amount of opaque material in reflected rather than transmitted light. This procedure would always eliminate the bias as far as the opaques are concerned, but if some one of the transparent minerals systematically mantled the opaque particles, the amount of this material relative to other transparent minerals would be underestimated in transmitted light.

The general case, in which neither mineral is opaque, is considerably more difficult and, I believe, more important. There is need of a good experimental study of the problem, and without such a study we are not likely to know just how serious it is. The difficulty arises because the analyst either does not or cannot confine his observations to the surface of the thin section. If the rock is so fine grained that individual particles are of the order of magnitude of imperfections in the surface (or depth of focus of the microscope), the lower limit of modal analysis has been reached. Even if we knew the appropriate corrections in the latter case, they would probably be so large that most of us would hesitate to use them.

¹ Min. Mag., 1952, vol. 29, p. 833.

It may be useful to point out in closing that what is involved is not grain size in any absolute sense. Rather, it is the ratio of grain size to thin-section thickness that governs the size of the bias. It may be calculated from table I, for instance, that particles of spherical radius 0.06 mm. will be subject to a 37.5 % overestimate in thin sections of standard thickness. If, however, the thickness of the thin section could be reduced by a factor of 3, the bias would be reduced to something less than 15 %. And if it were possible to prepare slides one-fifth of the standard thickness, the bias would be only 7.5 %.

SHORT COMMUNICATIONS

The rediscovery of churchite in Cornwall.

AFTER the lapse of just over one hundred years, the rare yttrium phosphate, churchite,¹ has been rediscovered in Cornwall, at Tretoil mine, about 5 miles north-west of Lostwithiel.

Churchite was first described by A. H. Church and named by C. G. Williams in 1865, the few known specimens having been collected some years previously, in Cornwall, by R. Talling, of Lostwithiel, the well-known Cornish mineral-dealer; but beyond revealing that it was near Lostwithiel, in a copper-lode, Talling never divulged the exact locality, which has so far remained unknown.

The similarity between the matrix of the old specimens and certain veinstone occurring at Tretoil mine and the fact that there are few copper-lodes near Lostwithiel and that two were worked at Tretoil mine up to about 1862, had led Sir Arthur Russell, who has in his possession what remains of Church's original specimens, to wonder whether this mine might possibly have been Talling's locality. Having examined Sir Arthur's specimens and also visited Tretoil several times, I was likewise struck by the similarity of the matrix and some of the veinstone at this mine. Both of us have searched for churchite on a number of occasions, hitherto without success, but on a visit to Tretoil last autumn I succeeded in collecting a small specimen of whose identity, even at the time, there was no doubt; subsequent examination confirmed that it is churchite. The matrix is almost identical with that of the old specimens, and the mineral itself, which is quite fresh, and was investing the side of a small cavity, is exactly similar; these facts would now seem to provide reasonable grounds for supposing that Tretoil mine was also the original locality and that Sir Arthur's guess was right.

*Dept. of Mineralogy,
University Museum, Oxford*

ARTHUR W. G. KINGSBURY

¹ See G. F. Claringbull and M. H. Hey, *Min. Mag.* 1953, vol. 30, p. 211, where the earlier and other references may be found, and where a new analysis is given.